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Process Development of BaZrO₃-BaCeO₃ Based Electrolytes for Proton-conducting Solid Oxide Fuel Cells

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Abstract

Solid oxide fuel cells (SOFCs) are electrochemical energy conversion devices which can convert chemical energy into electrical energy directly with high efficiency and fuel flexibility. The main challenge hindering the commercialization of SOFCs is the high operating temperatures (800-1000 °C) which pose heavy demands on materials and considerable challenges for thermal management. Therefore, to realize the practical application of SOFCs, research has been trending towards reducing the operating temperatures to low temperature (LT) range below 600 °C by reducing the electrolyte thickness and/or utilizing alternative electrolytes with higher ionic conductivity. Proton-conducting ceramics are regarded as promising electrolyte materials for LT-SOFCs since they show smaller activation energy for proton conduction and larger ionic conductivities at low temperature range than conventional oxygen-ion conducting electrolytes. However, the high processing temperatures and the lack of economical and scalable fabrication method for proton-conducting electrolytes have restricted the commercial development of protonic SOFCs. To address these problems, this thesis aims at developing economical and scalable methods to fabricate BaZrO₃-BaCeO₃ based proton conducting electrolytes at reduced processing temperatures.

A single-step slurry spray coating method has been demonstrated to prepare proton conducting BaCe_{0.7}Zr_{0.1}Y_{0.2}O₃ (BCZY) membranes on the pre-annealed porous anode substrates. The effects of sintering temperature on the electrolyte membrane and anode microstructure, proton conductivity of the resulted thin films, and their fuel cell performances have been investigated. Dense BCZY membranes with improved anode microstructure and good proton conductivity have been successfully obtained at reduced temperature using ZnO sintering aid. SOFCs using 20 μ m spray-coated electrolyte membranes gave a stable open circuit voltage (OCV) value of 1.03 V and a maximum power density of 362 mW/cm² at 650 °C when operated using hydrogen as fuel.

In order to realize a scalable and cost-effective fabrication of sub-micrometer scale proton-conducting electrolytes, chemical solution deposition (CSD) method has been proposed for the fabrication of electrolyte thin films. At first, a sol-gel spin-coating method has been demonstrated for the fabrication of a 200 nm-thick yttrium-doped barium zirconate (BZY) thin film without obvious through-film cracks. The stoichiometry of the BZY thin film was well-controlled and no Ba evaporation was observed due to the low processing temperature. Then a modified chemical solution deposition route has been developed to fabricate dense and crack-free BZY electrolyte thin films. A stable chemical solution was synthesized with the addition of several organic compounds. BZY thin film with good crystallinity can be obtained after annealing at 800 °C for 2 hours. BZY electrolyte thin film with a thickness of 500 nm was fabricated on anode substrate from a colloid solution. The OCV of the anode-supported cell with BZY thin film electrolyte was above 1 V, indicating a good gas tightness of the BZY thin film fabricated by CSD. Finally, rapid thermal processing has been explored as an alternative sintering schedule to further lower the sintering temperature. Dense, homogenous and crack-free BZY thin film with good crystallinity was obtainable after annealing at 700 °C for 1 hour. The low processing temperature and shorter annealing time allow the incorporation of chemical solution deposited BZY thin films into micro-SOFC devices. Compared to the sophisticated vacuum-based thin film deposition techniques, this cost effective and scalable CSD method is a promising way for mass production of electrolyte thin films for micro-SOFCs.

Chapter 1

Introduction

1.1 Background

Our modern societies are facing the problems of energy crisis, global greenhouse effect and environmental pollution caused by combustion of fossil fuels through conventional power generation technologies. To realize a more sustainable future, developing alternative efficient and environmental-friendly energy conversion systems has aroused increasing concerns [4].

Fuel cells, electrochemical energy conversion devices that directly convert chemical energy stored in fuel into electrical energy, have been considered as promising renewable and sustainable energy conversion systems. The direct transformation of energy from chemical form into electrical form gives fuel cells much higher energy conversion efficiency than conventional thermo-mechanical systems. Besides, fuel

cells almost give no emission of pollutants since the product from the electrochemical reaction between hydrogen and oxygen is pure water [5].

Fuel cells are typically classified according to the types of electrolyte material. There are five major types of fuel cells: polymer electrolyte membrane fuel cells, alkaline fuel cells, phosphoric acid fuel cells, molten carbonate fuel cells, and solid oxide fuel cells (SOFCs). Among the various types of fuel cells, SOFCs have drawn extensive attention because of their high efficiency, fuel flexibility, modularity and reliability. In addition, SOFCs utilize solid ceramic electrolytes, which obviates the need of corrosive liquids.

The main challenge that hinders the commercialization of SOFCs is the high operating temperatures. Conventional SOFCs with yttria-stabilized zirconia (YSZ) electrolyte need to operate at high temperature range of 800-1000 °C to achieve sufficient electrolyte conductivity and activate the electrode kinetics. These high operating temperatures impose heavy demands on materials and considerable challenges for thermal management. Therefore, current researches have been focused on reducing the operating temperature of SOFCs to low temperature (LT) regime below 600 °C. However, lowering the operating temperature of SOFCs would inevitably lower the fuel cell performance due to the increasing electrolyte resistance and electrode polarization. To reduce the electrolyte resistance for LT-SOFCs operation, one can either decrease the electrolyte thickness or use alternative electrolyte materials with high ionic conductivity. In order to reduce the electrolyte thickness, the SOFC configuration has changed from electrolyte-supported cells to

electrode-supported cells, especially anode-supported cells. The electrolytes typically have a thickness of tens of micrometers supported on the anode substrates. By further reducing the electrolyte thickness to nanometer scale, micro-SOFCs can be fabricated by MEMS process and thin film deposition techniques, which have great potential as small portable electronic devices.

1.2 Research Motivation

Proton-conducting ceramics are regarded as promising electrolyte materials for LT-SOFCs. Compared to conventional oxygen ion conducting electrolytes, proton-conducting electrolytes have lower activation energy for proton conduction and thus higher ionic conductivities at low temperature range. Among proton-conducting electrolyte materials, acceptor-doped barium cerate materials show highest protonic conductivity but poor chemical stability. Acceptor-doped barium zirconate materials have excellent chemical stability and high bulk proton conductivity, but the highly refractory nature of barium zirconate-based materials and large grain boundary resistance lead to lower total conductivity compared to doped BaCeO_3 materials. Solid solutions of BaCeO_3 and BaZrO_3 can encompass high proton conductivity and good chemical stability of the two materials. However, the sinterability is still not satisfying and high sintering temperatures up to 1550 °C are needed. The high processing temperatures lead to several detrimental effects, such as Ba evaporation, poor anode porosity, and unwanted electrolyte/electrode interface reaction.

The fabrication challenge for proton-conducting electrolytes is one of the reasons why current protonic SOFCs have lower performance compared to oxygen ion conducting SOFCs. Several approaches have been explored to reduce the sintering temperatures as well as increase the proton conductivity of BaZrO_3 - BaCeO_3 based materials. Addition of sintering aids and synthesis of ultra-fine powders by modified wet chemical routes are two typical ways. However, there is still a lack of scalable and economical fabrication methods for proton-conducting electrolyte film deposition.

Ceramic powder processing methods are low-cost and most commonly used techniques for the fabrication of electrolyte film on anode substrate. However, currently, most of the researchers utilize co-pressing and co-firing process, which is not applicable for large scale membrane fabrication and not suitable for industrial purposes. Other scalable techniques such as tape casting and electrophoretic deposition are not effective to fabricate cell with good performance. Thus, alternative, economical and scalable ceramic membrane fabrication techniques with the capability of large size cell preparation and potential for high quality and high performance are urgently needed.

Thin film deposition techniques such as pulsed laser deposition (PLD) and atomic layer deposition (ALD) are effective ways to circumvent the sintering problem and reduce the electrolyte thickness to sub-micrometer level. PLD has been utilized to fabricate electrolyte film for both anode-supported cells and micro-SOFCs. However, PLD is a high-vacuum deposition technique and is suitable for small-scale application. The process is costly and time consuming, and require sophisticated

equipment set up. Therefore, chemical solution deposition method is proposed in this research to fabricate sub-micrometer BZY electrolyte thin film due to its advantages of simplicity, cost effectiveness, scalability and easy control of film composition.

1.3 Research Objectives and Scope

The purpose of this study is to develop economical and scalable methods to fabricate proton conducting electrolytes at low processing temperatures. To achieve this, two specific objectives are set as follows:

1. To develop scalable powder-based membrane deposition process to fabricate electrolyte membrane for anode-supported SOFCs.
2. To develop chemical solution deposition process for the fabrication of sub-micrometer electrolyte thin films.

To achieve the objective of this project, the research scopes are outlined as follows:

For the first objective, the research scope covers:

1. Prepare BCZY membrane on pre-annealed porous anode substrate by spray coating method at reduced sintering temperature with ZnO as sintering aid.
2. Study the effects of sintering temperature on the electrolyte and anode microstructure.

3. Investigate the proton conductivity of the spray-coated electrolyte membrane and the fuel cell performance.

For the second objective, three parts of work have been implemented:

1. Develop an aqueous sol-gel process for the deposition of sub-micrometer BZY thin film combined with spin coating technique.

A systematic study is performed to investigate the process parameters including annealing temperature, sol concentration and heating rate. The resulted phase and microstructure of the BZY thin films are characterized.

2. Develop a modified chemical solution deposition process to fabricate BZY film on anode substrate.

BZY chemical solution with addition of dispersed BZY nanoparticles is prepared and the sintering process is carefully controlled to eliminate the drying and constraint sintering cracks of the thin film. The open circuit voltage of the anode-supported cell is measured to verify the gas-tightness of the film.

3. Exploit rapid thermal processing as the sintering strategy to fabricate dense BZY thin film at reduced temperature.

The precursor solution is modified to reduce the drying and sintering stress, and the heating process is optimized to obtain crystallized and dense BZY film with smooth and homogenous surface structure.

1.4 Thesis Outline

The remaining thesis includes the following chapters:

Chapter 2 provides a overall literature review of LT-SOFCs and proton-conducting electrolytes. Various fabrication methods for proton-conducting electrolytes are also reviewed.

Chapter 3 describes the experimental procedures in detail.

Chapter 4 demonstrates the fabrication of dense BCZY electrolyte membrane by spray coating method. The microstructure of electrolyte film and anode, the electrolyte membrane conductivity, and the fuel cell performances have been investigated.

Chapter 5 presents the fabrication of sub-micrometer BZY thin films by chemical solution deposition methods. Different chemical solution routes and heating processes have been investigated and employed for the preparation of BZY thin films. The crystallinity, microstructure, and composition of the films have been studied.

Chapter 6 provides the conclusions and suggests potential directions for future work.

Chapter 2

Literature Review

2.1 Solid Oxide Fuel Cells

2.1.1 Operation principle

SOFCs are solid-state devices using ion-conducting ceramic materials as electrolytes. A SOFC consists of three basic components: an anode (a fuel electrode), an electrolyte as ionic conductor, and a cathode (an oxidant electrode). The electrolyte layer must be fully dense to avoid short circuit and gas mixing, whereas the electrodes need to be porous to facilitate gas transportation.

Figure 2.1 schematically shows the operating principle of hydrogen-oxygen fuel cell with (a) oxygen ion conducting electrolyte and (b) proton conducting electrolyte. Hydrogen is supplied to the anode side as the fuel, and air is introduced to the cathode side as oxidant.

FIGURE 2.1: Schematic diagrams of SOFC with (a) oxygen ion conducting electrolyte and (b) proton-conducting electrolyte.

For the fuel cell with oxygen ion conducting electrolyte, oxygen reduction reaction takes place at the cathode side where oxygen molecules combine with the electrons and is reduced to oxygen ions. These ions migrate through the electrolyte to the anode side and hydrogen oxidation reaction occurs, forming water and releasing electrons. Meanwhile, electrons travel through the external circuit from the anode side to the cathode side, thereby generating electricity.

The electrochemical reactions in the fuel cell is described as follows:

Cathode: oxygen reduction reaction (ORR)

Anode: hydrogen oxidation reaction (HOR)

Overall cell reaction:

For the fuel cell with proton-conducting electrolyte, hydrogen is oxidized and split into protons and electrons at the anode side. The electrons travel through the external load circuit and then arrive at the cathode side. Meanwhile, the protons can transport through the electrolyte membrane to the cathode side where they react with oxygen molecules and the electrons to generate water.

2.1.2 Fuel cell performance

2.1.2.1 Thermodynamics

The maximum voltage which can be obtained for a fuel cell is determined by thermodynamics. Considering a fuel cell as a reversible system, the maximum

electrical work available for conversion into usable work is determined by the Gibbs free energy change associated to the fuel cell reaction.

$$W_{el} = \Delta G = -nFE. \quad (2.4)$$

where n is the number of electrons involved in the cell reaction; F is the Faraday constant; E is the reversible voltage of the cell.

The reversible voltage under standard-state is related to the standard-state Gibbs free energy change, and can be expressed by:

$$E^0 = -\frac{\Delta g_{rxn}^0}{nF} \quad (2.5)$$

For an ideal fuel cell, taking into account of reactant partial pressure and concentration, the reversible voltage of the fuel cell at given temperature and pressure is determined by the Nernst equation. For the reaction of a hydrogen-oxygen fuel cell, the Nernst equation appears to be:

$$E = E^0 - \frac{RT}{2F} \ln \frac{p_{H_2O}}{p_{H_2} \cdot p_{O_2}^{\frac{1}{2}}}. \quad (2.6)$$

where E^0 is the standard-state reversible voltage; R is the ideal gas constant; T is the fuel cell working temperature; F is the Faraday constant; p is the partial pressure.

2.1.2.2 Fuel cell performance

The performance of a SOFC can be evaluated by its current-voltage (I-V) curve, which shows the output voltage of a fuel cell at a given current density. The ideal fuel cell performance is defined by the theoretical voltage of a cell operated under reversible condition. However, when the current is drawn from the fuel cell, the output voltage starts to decrease from the theoretical value due to the irreversible losses in a fuel cell operation.

There are three major types of fuel cell losses, corresponding to three different loss mechanisms. They are:

Activation losses (η_{act}) due to the electrochemical reaction at the electrode;

Ohmic losses (η_{ohmic}) due to ionic and electronic conduction;

Concentration losses (η_{conc}) due to mass transport limitations.

Considering all the losses, the actual voltage output of a fuel cell is expressed as:

$$V = E_{thermo} - \eta_{act} - \eta_{ohmic} - \eta_{conc}. \quad (2.7)$$

A typical I-V curve of a SOFC based on Eqn. 2.7 is shown in Figure 2.2. Each of the three losses contributes to the characteristic shape of the fuel cell I-V curve. The activation losses usually happen in the low current regime; the ohmic losses become most apparent in the middle regime of the current; the concentration losses are dominant in the high current regime.

FIGURE 2.2: Schematic of current-voltage characteristics of a SOFC.

2.2 Low temperature SOFCs

The conventional SOFCs based on yttria-stabilized zirconia (YSZ) electrolyte usually operate at high operating temperatures (800-1000 °C), which is the main technical issue hindering the commercialization of SOFCs. The high operating temperatures may result in heavy demands on expensive ceramic materials for interconnection, require long start-up times, and may even lead to system degradation due to thermal stress [6]. Therefore, to realize the practical application of SOFCs, research has been trending towards reducing the operating temperature to low temperature (LT) range below 600 °C. The low operating temperature will allow the use of cheaper materials, simplify the cell and stack construction, and improve the long-term stability [7].

However, lowering the operating temperature of SOFCs would inevitably lower the fuel cell performance due to the increasing ionic resistance in electrolyte and sluggish electrode reaction kinetics, since both the ion transportation in ceramic electrolyte and the electrochemical reactions at the electrodes are thermally activated process.

The ohmic losses dominated by the electrolyte resistance is the main cause of the reduced fuel cell performance. It is generally accepted that the area specific resistance (ASR) of electrolyte should not exceed $0.15 \text{ } \Omega \cdot \text{cm}^2$ for its practical application for SOFCs [2, 8].

The ohmic losses from electrolytes can be expressed as:

$$\eta_{ohmic} = j \cdot ASR = j \cdot \left(\frac{L}{\sigma}\right). \quad (2.8)$$

where j is the current density; σ is the ionic conductivity of the electrolyte material; L is the length of the ionic transport path (electrolyte thickness).

Based on Eqn. 2.8, the electrolyte's ohmic losses is proportional to the ion transportation distance or inverse proportional to the ionic conductivity value of electrolyte. Therefore, reducing the electrolyte thickness or/and using alternative electrolyte materials with higher ionic conductivity can lower the electrolyte resistance. To reduce the electrolyte thickness, the SOFC configuration has changed from electrolyte-supported cells (2.3(a)) to electrode-supported cells, especially anode-supported cells (Figure 2.3(b)). The electrolytes typically have a thickness of tens of micrometers supported on the anode substrates. Anode-supported

SOFCs based on novel oxygen ion conducting electrolytes, such as doped ceria and stabilized bismuth oxide can achieve the low temperature operation at 450-600 °C [7].

FIGURE 2.3: Illustration of (a) electrolyte-supported SOFC and (b) anode-supported SOFC.

By reducing the electrolyte thickness to nanometer scale, micro-SOFCs can be fabricated based on MEMS (micro-electro-mechanical system) and thin film deposition techniques [1]. Due to the reduced ionic diffusion path length, the operating temperatures of micro-SOFCs can be reduced below 500 °C, and down to as low as 350 °C. Two micro-SOFC configurations, free-standing membrane and porous substrate supported type, are shown in Figure 2.4.

FIGURE 2.4: Schematic drawing of (a) a free-standing SOFC and (b) a thin film SOFC membrane on a porous substrate [1].

2.3 SOFCs with proton-conducting electrolytes

High oxygen-ion conductive electrolyte materials such as doped-ceria, doped-lanthanum gallate, and doped-bismuth oxide have been widely explored in the past decades

[7]. However, due to the high activation energy associated with oxygen-ion conduction, fuel cell performance drops rapidly at reduced temperature.

In alternative to oxygen-ion conducting electrolytes, proton-conducting ceramic materials, especially acceptor-doped perovskite-type oxides (ABO_3), have attracted extensive attention as promising electrolyte candidates for SOFC operation at low temperature range [2, 3, 9]. Due to the smaller activation energy for proton conduction through oxide lattice, the proton conducting oxides can achieve higher ionic conductivity at low temperature range compared to oxygen-ion conductors. Figure 2.5 shows the ionic conductivity of currently developed oxygen-ion conductors and proton-conducting Y-doped barium zirconate (BZY) in low temperature of 300-600 °C. The proton conductor shows a much smaller activation energy and higher ionic conductivity at low temperature range than oxygen ion conductors such as SDC, LSGM, and YSZ [2]. In addition, for SOFCs with proton-conducting electrolyte, water is generated at the cathode side, which can avoid fuel dilution at the anode side.

Proton-conducting SOFCs also present advantages when operating on hydrocarbon fuels. Considering methane as fuel, it can be converted to hydrogen via internal steam reforming in the presence of water. Compared to oxygen ion conducting SOFCs, protonic SOFCs have higher CH_4 conversion levels because of direct proton removal from the fuel [10]. Carbon coking issue can also be prevented since protonic SOFC operation disfavors the Boudouard Reaction which lead to carbon deposition [10, 11]. In dry environments, methane can undergo a dehydrogenation reaction to produce hydrogen and other high-molecular hydrocarbons without CO

FIGURE 2.5: Comparison between the ionic conductivities of proton-conducting BZY and the current high performing oxygen-ion conductors, SDC, LSGMs, and YSZ [2].

and CO_2 generation, as shown in Eqn. 2.9 and 2.10 [9, 12]. For low temperature operation, the catalysis of anode material need to be optimized for efficient reaction.

2.3.1 Conduction mechanism of proton-conducting electrolyte

The general structure of proton conducting oxides is acceptor-doped perovskites with the formula ABO_3 . The A cation is an alkaline earth element, usually Ba or Sr, while the B cation is a tetravalent transition metal or a rare earth element,

usually Zr or Ce. Oxygen vacancies can be created by partially doping the B site with trivalent cation, such as Y, Yb, In, and Nd.

Exposing the perovskite-type oxides to hydrogen and/or water vapour containing atmosphere, mobile protons are incorporated into the perovskite structure by replacing oxygen vacancies with hydroxide ions. Protonic defects are formed mainly by the reaction of dissociative adsorption of water. In Kröger-Vink notation this reaction is given as,

Proton migration occurs via a Grotthuss-type mechanism by proton hopping. The detailed proton migration process includes proton rotational diffusion around oxygen ion and proton transfer to the nearest oxygen ions, as shown in Figure 2.6. This easy migration results in lower activation energy and higher conductivity compared to oxygen-ion conductors.

FIGURE 2.6: Proton conduction mechanism: rotational diffusion and proton transfer [3].

Due to the presence of oxygen vacancies in perovskite structure, proton-conducting oxides also show oxygen ion conductivity in certain conditions. In addition, p-type electronic conduction appears since oxygen incorporation produces holes, according to following reaction:

The predominant charge carrier in this class of materials depends on dopant, temperature, oxygen partial pressure, and hydrogen partial pressure. According to the reaction equation, oxygen ion conduction is predominant at low oxygen partial pressure condition in the complete absence of water vapour and hydrogen. Electronic (p-type) conduction dominates at high oxygen partial pressure condition. Generally, protons are the main charge carriers in the presence of water vapour and/or hydrogen at reduced temperature. Research has found that proton conduction is predominant below 600 °C in the presence of water vapour and/or hydrogen for $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ material [13]. For $BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$ material, proton conduction is is predominant below 700 °C [14].

2.3.2 Proton-conducting electrolyte materials

The pioneering work of proton-conducting electrolyte materials was done by Iwahara et al. in 1981 [15]. They demonstrated that doped- $SrCeO_3$ exhibited proton conduction with the presence of water or hydrogen-containing atmosphere at high temperature. Among the proton-conducting ceramics, acceptor-doped

BaCeO₃ shows the highest performance with large proton conductivity. A proton-conducting SOFC with Y-doped BaCeO₃ (BCY) electrolyte has shown high performance with a power output of 900 mW/cm² at 400 °C [16]. However, doped barium cerate materials are not suitable for practical SOFC application because of the poor chemical stability in acidic gases and humid atmosphere [17]. The high basicity of BaCeO₃ results in the reaction with CO₂ and water and decomposition into BaCO₃ and Ba(OH)₂ or CeO₂, as shown in Eq. 2.13 and 2.14.

In contrast, barium zirconate based materials show excellent chemical stability in rather aggressive environments [18]. Among barium zirconate materials, BaZr_{0.8}Y_{0.2}O_{3-δ} (BZY20) shows the largest proton conductivity in the literature [19] and it has been reported that the bulk conductivity of BZY20 is even larger than that of doped barium cerate materials [20]. The results indicate BZY is a promising proton-conducting material for practical applications. However, the highly refractory nature together with the large grain boundary resistance are two main drawbacks for barium zirconate-based materials. The poor sinterability leads to small grain size and large grain boundary density in sintered barium zirconate, resulting in much lower conductivity compared to doped barium cerate samples [18, 21]. Moreover, because of its highly refractory nature, the fabrication of dense

electrolyte layers for doped barium zirconate remains a significant challenge. Extremely high heat treatment temperatures (around 1700 °C) are usually required to sinter dense electrolyte layers [22–24]. Such high sintering temperatures may cause undesired chemical reactions in electrolyte/electrode interfaces and makes it difficult to retain the porous microstructure of electrode.

Solid solutions of BaCeO₃ and BaZrO₃ can encompass the high proton conductivity and good chemical stability of the two materials. The partial substitution of Ce by Zr is an effective approach to enhance the chemical stability while maintain adequate proton conductivity of the material. Zuo et al. [25] developed a solid solution of BCY and BZY, BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-δ} (BZCY7), with adequate conductivity and sufficient chemical stability at low temperature range, which could be a promising electrolyte for proton-conducting SOFC operating at low temperature.

Numerous strategies have been explored to enhance the sinterability and increase the total conductivity of doped barium zirconate materials. One of the approaches to improve the sinterability is to synthesize nanopowders by modified wet chemical routes, which can promote densification and facilitate sintering at lower temperatures. Khani et al. [26] synthesized BZY nanosize powders by low temperature chemical synthesis method, and the BZY pellets sintered at 1500 °C can reach a relative density up to 95%.

The addition of sintering aids have also been explored to reduce the sintering temperature and enhance the grain growth. ZnO addition was effective to enhance the densification of BZY material [27, 28]. BZY20 adding 1 wt% ZnO can achieve 96% relative density after sintering 10 h at 1325 °C [28]. Zn atom enters into the

lattice and substitute in the B site of the ABO_3 structure. This may cause proton trapping and result in lower ionic conductivity. With the addition of NiO as a sintering aid, dense BZY20 pellets with large grain sizes of $5\text{ }\mu\text{m}$ can be obtained after sintered at $1400\text{ }^\circ\text{C}$ [29]. The NiO-modified BZY20 shows proton conductivity of $3.3 \times 10^2\text{ S/cm}$ at $600\text{ }^\circ\text{C}$. By adding a sintering aid of volatile lithium compound, dense BZY20 samples can be obtained with sintering temperature of $1600\text{ }^\circ\text{C}$ [30]. Though the grain growth was limited, the total proton conductivity was still acceptable.

The addition of co-doping elements can modify the sintering properties of $\text{BaZrO}_{3-\delta}$ based materials. Fabbri et al. [31] have developed $\text{BaZr}_{0.7}\text{Pr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ as a easily sintered highly proton-conductive material by partially substituting the Zr site with Pr element. Sun et al. [32] reported the co-doping of Y and In into BaZrO_3 would lead to an improved sinterability. They also found $\text{BaZr}_{0.8}\text{Y}_{0.15}\text{In}_{0.05}\text{O}_{3-\delta}$ had good chemical stability and sufficiently high total conductivity.

Pergolesi et al. [20] have presented the highest proton conductivity for highly textured and epitaxial BZY thin film grown on (100)-oriented MgO substrate by pulsed laser deposition (PLD). The grain boundary blocking effects were excluded due to the epitaxial crystallinity of BZY thin films. The BZY thin film can reach to a high proton conductivity of 0.01 S/cm at a low temperature of $350\text{ }^\circ\text{C}$ with the absence of grain boundaries.

Generally, for proton-conducting electrolyte, dense structure with large grain size is preferred, since large grain size leads to low grain boundary density and high

proton conductivity value. For nanoscale electrolyte thin film, the film crystallinity, microstructure and composition can affect the film conductivity. Epitaxial film shows highest proton conductivity; increased crystallinity, less grain separation, and less barium deficiency result in higher conductivity value [33–35].

2.3.3 Electrodes for proton-conducting SOFCs

To utilize proton-conducting electrolytes in LT-SOFCs, anode-supported cell is the most commonly used structure. The anode material is usually the mixture of Ni with electrolyte material. The anode morphology plays important role to its electrochemical performance. Large specific surface area lead to large triple phase boundary (TPB) and fast reaction rate. Therefore, the anode substrate should possess sufficient porosity to ensure gas diffusion and reaction at TPB. In proton-conducting SOFCs, chemical reactions at the electrode/electrolyte interfaces have been reported due to the high sintering temperature of electrolyte material. The interface reactions lead to the formation of insulating phases, which limit the ionic transportation and result in increased electrode polarization [36].

For protonic SOFCs, the cathode reaction is more complicated than that in oxygen ion conducting SOFCs. The cathode elementary reaction steps involves oxygen dissociative absorption, diffusion, and reduction, proton migration, and the water formation and evaporation. The cathode should have porous structure and good adhesion to electrolyte to allow gas diffusion and ensure sufficient reaction site. The most desirable cathode materials are triple-conducting oxides which can conduct proton, oxygen ion and electron simultaneously. In this way,

the electrochemical active site can be extended to the entire cathode, thereby increasing the fuel cell performance. Recently, several high-performance triple-conducting oxide cathodes have been explored. Layered perovskite cathode material, $\text{NdBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5+\delta}$ (NBSCF) has been developed as triple-conducting cathode material for protonic SOFCs and showed excellent compatibility with proton-conducting electrolyte [37]. A recent work presented $\text{BaZr}_{0.1}\text{Co}_{0.4}\text{Fe}_{0.4}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BZCFY) as triple-conducting cathode by doping of transition metals into proton-conducting oxide $\text{BaZr}_x\text{Y}_{1-x}\text{O}_{3-\delta}$. The material shows excellent catalytic activity and sufficient conductivity of triple charge carriers, and impressive electrochemical performance was reported at low operating temperature. Fan et al. [38] have demonstrated layered structured $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ (LNCO) showing intrinsic conduction of oxygen ions and electrons, and extrinsic proton conduction. The LNCO cathode is regarded as promising simple and low cost cathode material with triple-conduction and good ORR activities for protonic SOFCs.

2.3.4 Proton-conducting SOFCs

Proton-conducting SOFCs based on Y-doped BaCeO_3 (BCY) electrolytes can obtain high performance due to the high ionic conductivity of BCY material. Ito et al. [16] demonstrated a hydrogen membrane fuel cell with a thin BCY electrolyte ($0.7\text{ }\mu\text{m}$) coated on a Pd hydrogen membrane. It exhibited high power output of 0.9 and 1.4 W/cm^2 at 400 and 600 °C. However, BCY is not suitable for long-term operation since BCY is chemically instable and easy to react with water vapour and CO_2 during cell operating condition.

Bilayer electrolytes consisting of BCY covered with BZY protective layer at cathode side have been applied to improve the chemical stability without significantly impairing the fuel cell performance. E Fabbri et al. [39] firstly proposed the bilayer structures and fabricated a 1 mm BCY pellet covered by 1 μm BZY film grown by PLD. The BZY layer can protect BCY against CO_2 and the conductivity of the bilayer electrolyte is similar to the BCY pellet. Qian et al. [40] have demonstrated the fabrication of anode-supported SOFCs with BCY-BZY bilayer electrolytes. The cell with bilayer electrolyte showed a comparable performance with good long-term stability.

BaCeO_3 - BaZrO_3 solid solution materials have acceptable chemical stability and sufficient ionic conductivity in low temperature range. The fuel cell with a BZCY7 electrolyte film was fabricated by co-pressing process and the cell achieved peak power densities of 148 and 56 mW/cm^2 at 600 and 500 $^\circ\text{C}$ [25]. BaCeO_3 - BaZrO_3 co-doped with Y and Yb (BZCYYb) has been reported to have higher proton conductivity compared to BZCY at low temperature range [41, 42]. SOFCs based on BZCYYb electrolytes have been widely developed with modified cathode materials. The fuel cell with 15 μm BZCYYb electrolyte and triple-conducting layered perovskite cathode NBSCF exhibit a peak power density of 1.61 W/cm^2 at 750 $^\circ\text{C}$ with long-term stability for 500 h [37].

Doped barium zirconate materials are promising electrolyte candidates since they exhibit excellent chemical stability with high bulk conductivity. However, due to the poor sinterability, fabrication of barium zirconate-based anode-supported fuel

cells is extremely challenging. Several powder-based sintering methods have been explored for the preparation of BZY electrolyte films on anode substrates.

Sun et al. [43] fabricated BZY electrolyte membrane with 20 μm thickness on NiO-BCZY anode by co-pressing method without the addition of sintering aid, but the SEM cross-section images showed a small grain size of the BZY membrane and inadequate anode porosity. The proton-conducting SOFC with SSC-SDC as cathode only reached a maximum power density of 70 mW/cm^2 at 600 $^\circ\text{C}$.

Bi et al. [44] have presented higher fuel cell performance by developing an ionic diffusion strategy for the preparation of BZY electrolytes for anode-supported SOFCs. This strategy utilized the high sinteractivity of In-doped BaZrO_3 and Y migration from anode substrate to the electrolyte part, forming a dense BZY electrolyte film after firing at 1450 $^\circ\text{C}$. The cell achieved good performance with a maximum power density of 169 mW/cm^2 at 600 $^\circ\text{C}$.

Preparing BZY electrolyte thin films by PLD is an effective approach to avert the sintering problem and reduce the film thickness. Pergolesi et al. [45] have fabricated fully dense BZY electrolyte films with 4 μm thickness by PLD on conventional sintered NiO-BZY anodes. During fuel cell test, the in situ reduction of NiO to Ni can enable anode to obtain sufficient porosity. With a 100 nm porous LSCF thin film as cathode functional layer and LSCF-BCYb composite as cathode, the anode-supported SOFC produced a maximum power density of 110 mW/cm^2 at 600 $^\circ\text{C}$. This work indicated the possibility to fabricate dense BZY electrolyte thin film by PLD at low temperature of 600 $^\circ\text{C}$.

Duan. et al. [11] have reported their great contributions in the development of proton-conducting SOFCs, with the improvement in both fabrication process and cell performance. They demonstrated the use of sintering agents such as nickel oxide and copper oxide can effectively decrease the sintering temperature to 1400 °C and enhance the proton conductivity of doped BaZrO₃ electrolyte. The fuel cells were fabricated in one step directly from the raw precursor oxide, which simplified the fabrication process and can be applied to large-scale production. With the novel triple conducting cathode material BCFZY designed for proton-conducting electrolytes, the fuel cells achieved high power output of 445 mW/cm² on H₂ and 142 mW/cm² on CH₄ at 500 °C with long term stability for 1400 h.

Recently, promising results have also been obtained in developing micro-SOFCs for small portable electronic devices. Shim et al. [46] fabricated free-standing micro-SOFCs with nanoscale BZY electrolytes deposited by atomic layer deposition (ALD) and PLD techniques. Porous platinum thin films deposited by sputtering were incorporated as the electrodes. The fuel cells achieved high performance with peak power densities of 136 mW/cm² at 400 °C for cell with ALD BZY electrolyte and 120 mW/cm² at 450 °C for PLD BZY cell.

Su et al. [47] demonstrated a cup-shaped free-standing micro-SOFC fabricated by silicon micromachining process with BZY membrane electrolyte deposited by PLD technique. The active membrane area of the cell was greatly increased with the design of changing the flat BZY electrolyte thin film into 3D structure. The silicon substrate was pre-patterned with cup-shaped trenches, then a 300 nm BZY thin film was deposited by PLD. The performance of the fuel cell array showed a high

OCV and the power output was increased from the additional active membrane area.

Kim et al. [48] reported the fabrication of a 3-D crater patterned proton-conducting micro-SOFCs architecture by a novel nonlithographic nanospherical patterning method. The 120 nm thick BZY electrolyte thin film was deposited by PLD and porous Pt was deposited by sputtering to serve as the cathode and anode. The 3D structured fuel cell achieved a peak power density of up to 186 mW/cm² at 450 °C.

The highest performance of proton-conducting micro-SOFCs was reported by Li et al. [49] with the improved cathode reaction. By inserting an 8 nm GDC cathodic interlayer between the BZY electrolyte and porous platinum cathode, the power density of the silicon-based micro-SOFCs reached 445 mW/cm² at 425 °C. The impressive performance was attributed to the extended cathode reaction sites with the mixed oxygen-ion and proton conduction in GDC interlayer.

2.4 Electrolyte film deposition

To achieve the low temperature operation of SOFCs, electrolyte films with reduced thickness should be fabricated to lower the electrolyte resistivity. By using the electrolyte films with micrometer thickness, anode is usually assigned as the mechanical supporting substrate, and the anode supported structure is the most common cell configuration for SOFCs. By reducing the electrolyte thickness to submicrometer scale, micro-SOFCs with free-standing electrolyte membranes can

be fabricated by silicon-based MEMS process, which have great potential as small portable electronic devices. Different thin film fabrication technologies have been employed to prepare micrometer, sub-micrometer even nanometer electrolyte membranes for SOFCs. In this section, several electrolyte film deposition techniques will be reviewed.

2.4.1 Ceramic powder processing technique

Ceramic powder processing methods can be used for preparing dense electrolyte films with thickness of a few tens micrometer. Dry pressing, spray coating, tape casting, and electrophoretic deposition have been widely used for the preparation of dense electrolyte on porous electrode substrate.

Co-pressing is a commonly used ceramic powder processing technique in laboratory scale. During the cell fabrication process, usually anode powders are dry pressed in ad die to obtain the anodic substrate. Then a layer of electrolyte powders is distributed on the substrate and pressed under high pressure. Finally, the bilayer structure is sintered at high temperature to form the dense electrolyte membrane on porous anode substrate. The powder distribution must be as even as possible to ensure a uniform pressure distribution on the pressed part. Co-pressing has been widely employed in laboratory to fabricate cell components [50]. A thin BCZYYb membrane (15 μm) was successfully prepared by Ding H. et al. [51] used co-pressing and co-firing technique on the porous anode substrate. However, some technique drawbacks associated exist: It is difficult to get homogeneously covered electrolyte layer on the porous anode substrate, and, therefore, requires

precious technique skill and auxiliary processing. The non-uniform dispersal of electrolyte powders may lead to electrolyte defects, like delamination and crack, those are detrimental to cells' eventual performance [51]. In addition, this method also has technique limits for fabrication of large scale membranes [52].

Tape Casting is a suitable technique to fabricate large-scale cell components from ceramic powders [53]. Ceramic powders, organic binder and plasticizer are dispersed in a solvent to form the viscous slurry. The slurry is then laid onto a carrier by passing it under a movable doctor blade. Multi-layer tapes can be fabricated by subsequently casting of layers on the top of the substrate layers. During the drying and sintering process, the shrinkage rate of the different materials should be totally matched throughout the binder burn-out and sintering temperature regime. Among various techniques, tape casting is the most favourable method for large scale cell fabrication. A recent work by Marrony M. et al. [54] prepared large size planar anode supported protonic SOFC up to 50 cm² with BaCe_{0.8}Zr_{0.1}Y_{0.1}O_{3-δ} electrolyte by tape casting method. However, tape casting method has several disadvantages. Tape casted SOFC normally presented insufficient electrochemical performances due to the required thicker electrolyte layer and scale-up effect: the maximum power output of only 150 mW/cm² was obtained at 600 °C in Marrony's report [54].

Electrophoretic deposition involves the deposition of charged powder particles from a suspension onto a metallic electrode or a conductive substrate under an applied electric field [55]. This technique has the advantages of a short formation time and little restriction on the shape of the substrate. The equipment of electrophoretic

deposition is relatively simple and low cost. However, the high shrinkage associated with the binder burn-out is challenging for application.

Spray coating is an economical and scalable process with flexible film thickness control. Spray coating can serve as an alternative, economic membrane fabrication techniques with the capability of large size cell preparation and potential for high quality and high performance. In spray coating process, the suspension of ceramic powders is coated on the substrate by spraying, then dried, preheated, and finally sintered at high temperature. This cycle can be repeated for several times to achieve a desired film thickness.

Spray coating has been widely used in fabricating the cell components of oxygen ion conducting SOFCs, including electrolyte, electrodes, and interconnects because of its low cost, process simplicity and ease of thickness controlled by repetitions of spraying. It is also flexible to integrate with many other advanced technologies, such as spray pyrolysis coating [56] and plasma spray coating [57], to modify the film quality. However, it has not yet received enough attention in the application for proton-conducting SOFCs, especially for fabrication of Zr element involved proton-conducting electrolytes which has improved chemical stability, likely due to the high refractory nature and low sintering activity of proton-conducting oxides that requires extremely high sintering temperature to obtain a gas impermeable membrane.

Table 2.1 provides a brief summary of current scalable powder-based fabrication processes for proton-conducting electrolyte membranes. However, the fuel cell

TABLE 2.1: A brief summary of scalable powder-based fabrication processes for proton-conducting electrolyte membranes

Electrolyte material	Fabrication process	Fabrication condition	Peak power density	Refs
BaCe _{0.7} Zr _{0.1} Y _{0.2} O _{3-δ}	tape casting	1400 °C 9 h	150 mW/cm ² at 600 °C	[58]
BaCe _{0.9} Y _{0.1} O _{3-δ}	electrophoretic deposition	1550 °C 2 h	174 mW/cm ² at 650 °C	[59]
BaZr _{0.8} Y _{0.2} O _{3-δ}	dip coating	1450 °C 6 h	70 mW/cm ² at 650 °C	[60]
BaCe _{0.7} Zr _{0.1} Y _{0.2} O _{3-δ}	suspension spray	1400 °C 5 h	207 mW/cm ² at 650 °C	[61]

performance of the presented results is still not satisfactory. Further efforts on improving the fabrication process and cell performance is necessary.

2.4.2 Thin film deposition technique

In this section, various techniques for sub-micrometer thin film deposition is reviewed. The working principles of several vacuum-based deposition techniques and chemical solution-based technique are elaborated.

PLD is a physical vapor deposition technique in which the desired films are deposited by ablating the target of the materials with a high-energy pulsed laser beam [62]. PLD has gained considerable attention for the preparation of dense electrolyte thin films due to the excellent control of the crystallinity and morphology of the deposited films with conserving the stoichiometry of the complex materials. In the PLD process, the pulsed laser impinges on the target material to form ejected plume with material plasma. The ejected vapor or plume is then deposited on the substrate and form thin film. The characteristics of the deposited films are influenced by various deposition parameters, such as wavelength, power density, substrate temperature, and target to substrate distance.

Sputtering can be classified as direct current (DC) sputtering and radio frequency (RF) sputtering depending on the power supply. In the sputtering process, material is ejected from a solid target by bombardment the target with energetic gas ions. Physical sputtering is driven by momentum transfer between the high kinetic energy ions and atoms in the target materials. The RF sputtering technique has been widely applied for the deposition of electrolyte thin films such as YSZ and GDC.

Chemical vapor deposition (CVD) is a chemical process whereby gaseous precursors react and/or decompose to produce the desired film on the substrate surface. As a modified CVD technique, ALD has gained great attention to fabricate extremely thin electrolyte films [63]. In ALD process, thin film is grown on the substrate by exposing the surface to gaseous precursors alternately. The precursors react with the surface in a self-limiting manner, so that the film is build one atomic layer after another. Dense YSZ electrolyte thin films have been grown by this method and utilized for micro-SOFC with novel architecture [64].

Vacuum deposition techniques can produce dense electrolyte thin films with high quality. However, these techniques are costly and require sophisticated equipment set up, and the process is time consuming. Thus, their implementation in large-scale SOFC manufacture is challenging.

Chemical solution deposition (CSD) is a solution based film deposition technique [65]. CSD is regarded as a potential method for mass production of SOFC components due to its advantages of scalability, cost-efficiency and flexibility. CSD process begin with the synthesis of solution with the organic/inorganic precursors

of metal cations together with solvents and some necessary solution modifiers. Next, the prepared solution can be deposited on the substrate by several different techniques, such as spinning, dipping and spray coating. The desired crystalline film is formed by the following thermal treatment. A variety of process parameters need to be controlled during each steps. The details of CSD will be reviewed in the next section.

2.5 Chemical solution deposition

2.5.1 CSD process

CSD method introduces three major types of solution methods along with several others; these divisions are based on solution chemistry (table 1). The three major methods are sol-gel, chelate and metal-organic precursor methods [66].

Sol-gel process typically involves metal alkoxides as precursors and alcohols as solvents. The commonly used alcohols are methanol, ethanol, 2-methoxyethanol, 1-3 propanediol, etc. The sol-gel solution undergoes hydrolysis-condensation reactions which leads to the formation of polymeric networks occurring through the generation of small particle resulting into colloidal suspension (sol), followed by the formation of continuous network in liquid matrix (gel).

The formation of sol and gel is aided by addition of water, base and acid; base and acid act as catalyst. The serious drawback of this method is the moisture sensitivity of some reactants. Therefore, sometimes difficulty appears during preparation

of the solution in open atmosphere because of atmospheric moisture.

Although alkoxide-alcohol system (sol-gel) systems are very successful to produce powder, it is difficult to keep control over the process due to uncontrolled hydrolysis and co-condensation reactions. Therefore, to replace the highly reactive alkoxide system, cations with complexing or chelating ligands are used as precursor materials. Chelate process employs metal carboxylate, -diketonate, or alkoxides as precursor materials. Acetic acid and acetylacetone are generally added to the precursors. Acetic acid plays dual role as chelating and bridging agents to reduce the crosslinking reaction, while acetylacetone acts as chelating agent and stabilizer of colloidal particles. This chelating agent partially replaces alkoxide ligand which blocks hydrolysis site, thereby prevents rapid reaction rate. Since the acetate ligands are bidentate in nature and sterically larger than alkoxy group, the reaction product with acetate groups is less susceptible to water. So, cross linking reaction (hydrolysis and condensation reactions) become less progressive.

The third general classified solution synthesis method is metallo-organic deposition (MOD). Long chain carboxylate compounds, e.g., lead 2-ethylhexanoate, titanium dimethoxy dineodecanoate, and zirconium neodecanoate are used as precursors. The organic moieties of long chain compounds enhance dissolution tendency and concomitantly hinder hydrolysis tendency. They are normally dissolved in common solvent such as xylene. As these precursors are water-insensitive and non-reactive to one another, they do not undergo any structural or chemical change. This process is the simplest one among the three methods. The disadvantage lies in

its long chain moieties because these disrupt the film during decomposition upon heat treatment.

There are several other routes such as Pechini method, aqueous solution, citrate, nitrate routes, aqueous method, combined colloidal-CSD method, etc.

After the precursor solution is prepared, one or several liquid layers can be coated on the substrate and then heat treated to form the desired material. The most common coating techniques are spin coating, dip coating and spray coating, as illustrated in Figure 2.7.

FIGURE 2.7: Schematic drawing of (a) spin coating, (b) dip coating, and (c) spray coating.

Spin coating is a simple procedure used to deposit uniform thin film on flat substrate. Typically, the coating substrate is held in place by vacuum chuck, and the chemical solution is dispensed onto the substrate. The substrate is then accelerated rapidly to the desired rotation speed. The excess liquid is spread out from the substrate due to the action of centrifugal force, leaving a uniform liquid thin film on the surface of the substrate. Several parameters, such as the spin speed, coating time, as well as the solution viscosity influence the thickness of the coating film.

Dip coating is a solution deposition technique allowing film coating on complex shaped substrate with large area. In this process, the film is formed through a liquid entrainment process. The general steps include the immersion and withdrawal of the substrate, film formation, and solvent evaporation. Starting with immersion of the substrate, a coherent liquid film is entrained on withdrawal of the substrate from the coating fluid, which then consolidates by drying and accompanying chemical reactions.

Spray coating represents the process based on transformation of a liquid precursor into a fine aerosol by atomizer or nebulizer. With the help of carrier gas, the fine droplets are carried into the coating chamber and then deposited on a heated substrate surface by gravity, or by the electrostatic field.

After film formation, a heat treatment process is necessary to obtain the crystalline and dense thin film. The process involves in removal of organic species, pyrolysis, densification, and crystallization. The organic removal and pyrolysis process is typically carried out at lower temperature of 200-400 °C and usually a hot-plate is used. Densification and crystallization are carried out at high temperature using furnace or rapid thermal annealing. The as-deposited film is converted into the crystalline film on the basis of the structural rearrangement process. Atomistic rearrangement, gel network rearrangement, structural relaxation, nucleation and growth are the general steps occurring in the process. By the careful control of heat treatment schedule, thin films with different crystallinity, microstructure and orientation can be obtained.

2.5.2 CSD of SOFC electrolyte

CSD can be an effective way to fabricate SOFC electrolyte thin film for low-cost and large-scale production. The YSZ electrolyte thin films fabricated by CSD have demonstrated high fuel cell performance. Oh et al. [67] have successfully deposited dense and gas-tight bilayer electrolyte with 100 nm YSZ thin film and 400 nm GDC thin film on a NiO-YSZ anode substrate by CSD. The entire fuel cell exhibited good performance with OCV above 1 V and peak power density of 1.3 W/cm² at 650 °C. This excellent electrochemical performance demonstrates that CSD can be an alternative method to fabricate electrolyte thin films for LT-SOFCs.

The chemical solution deposited proton-conducting BZY thin film electrolyte was firstly demonstrated by Schneller et al. [68]. The BZY20 precursor solution was prepared by metallo-organic decomposition methods from barium propionate, zirconium tetrabutoxide butanol complex and yttrium acetate hydrate. After multiple spin coating on platinized silicon substrate, the film was crystallized at 900 °C, forming a 630-nm-thick dense BZY20 film. The proton conductivity of the BZY20 film measured by impedance spectroscopy was, however, much lower compared with the bulk samples. Somroop et al. [69] used electrostatic spray deposition (ESD) to fabricate BZY thin films from the chemical solution. The BZY thin films were deposited on YSZ substrate by ESD technique with optimized precursor solution and process parameters. The perovskite BZY films were obtained after annealing at 1350 °C for 10 h.

However, the fabrication of proton-conducting electrolyte thin films by CSD method

has not been widely explored. Currently, there is no work demonstrating proton-conducting electrolyte prepared by CSD as electrolyte for SOFC application. The process development, parameter study and microstructure optimization have not been thoroughly investigated. What's more, the utilization of chemical solution deposited electrolyte thin films in micro-SOFCs has not been explored.

2.6 Chapter Summary

Proton-conducting oxides are regarded as promising electrolyte materials for LT-SOFCs. However, the refractory nature of these materials make it difficult to fabricate high performance protonic SOFCs. Currently, the lack of economical and scalable fabrication method has retrained the commercial development of protonic SOFCs. The electrolyte film fabrication techniques including powder-based deposition techniques and sub-micrometer thin film deposition methods have been reviewed in this chapter.

Powder-based processing techniques can be utilized to fabricate micrometer thick electrolyte films on anode substrates. Several powder-based techniques, such as co-pressing, tape casting, and spray coating, have been compared. Among them, spray coating method offers advantages of low cost, salability, and flexible film thickness control. Therefore, in this thesis, spray coating method will be explored to fabricate dense proton-conducting electrolyte film with micrometer thickness on anode substrates for LT-SOFCs. The process parameters, electrolyte conductivity, and cell electrochemical performance will also be investigated.

Chemical solution deposition methods are wet chemical processes starting from the prepared precursor solution. CSD methods can produce thin film with sub-micrometer thickness, which can reduce the electrolyte resistance for LT-SOFC application. Compared to other vacuum-based thin film deposition methods, CSD methods are cost-effective and can be scaled up for large area deposition. In addition, the sintering temperatures in CSD are much lower than powder-based techniques. However, the fabrication of electrolyte thin film for anode-supported SOFCs by CSD is challenging due to the large anode substrate roughness and the cracks of electrolyte film after sintering. For the utilization of CSD thin films in Si-based micro-SOFCs, the large film residual stress during drying and sintering impedes the integration into MEMS process. The work of fabricating BZY electrolyte thin film by CSD methods consists of three parts. In the first part, an aqueous sol-gel process is developed to demonstrate the feasibility of fabrication BZY thin film by CSD. The second part is dedicated to develop chemical solution deposited BZY film on anode substrate. BZY chemical solution with addition of BZY antiparticle is prepared and the sintering process is controlled to prevent cracks. In the third part, the precursor solution is modified and the sintering temperature is further reduced in order to fabricate low-stress BZY film for micro-SOFC application.

Chapter 3

Experimental details

3.1 Spray coating of BCZY electrolyte for anode-supported SOFCs

3.1.1 BCZY electrolyte powder preparation

The BCZY electrolyte powder was synthesized by a co-precipitation method by using $(\text{NH}_4)_2\text{CO}_3$ as the co-precipitant for the low solubility of separated carbonate or basic carbonates. The other rationales for choosing $(\text{NH}_4)_2\text{CO}_3$ as the co-precipitant are the low cost and low decomposition temperature of the remained precipitant. The cation ionics (Ba^{2+} , Zr^{4+} , Ce^{3+} and Y^{3+}) were dissolved in deionized water using the corresponding nitrate salts from Sigma-Aldrich (Singapore). The $(\text{NH}_4)_2\text{CO}_3$ was also dissolved in water in another beaker. The prepared cation solution was then added into the carbonate solution with vigorous stirring. The

molar ratio of $(\text{NH}_4)_2\text{CO}_3$ to all cations was set as 2.5:1 to fully precipitate the cations, and the final pH value of mixture was around 8. The white precipitates were then collected by filtration with suction after 2 h stirring, followed by drying in an oven of 100 °C for overnight. Then the dried precursor was annealed at 1100 °C for 3 hours to get well crystallized BCZY target powders.

3.1.2 Spray coating of BCZY electrolyte and sintering of electrolyte/anode half-cell

BCZY electrolyte layer on the porous anode substrate was obtained by the spray coating method. The detailed procedures of anode support and electrolyte spray coating are schematically illustrated in Figure 3.1.

The porous anode substrate composed BCZY and NiO powder in a weight ratio of 40:60. They were mixed together with pore former-activation carbon and ball milled in ethanol solvent for 24 hours and dried on hot plate at 80 °C. Then the dried mixed powder was dry-pressing at 200 MPa for 3 minutes to get green pellets with 24 mm diameter and thickness around 1 mm. All the collected pellets were calcined at 900 °C for 2 hours to enhance the mechanical strength as support for BCZY spray deposition.

The BCZY suspension was first synthesized by mixing of BCZY powder (with and without 1 wt.% ZnO sintering aid), ethanol solvent, polyvinyl alcohol (PVA) binder, dibutyl phthalate (DBP) and polyethylene glycol (PEG) plasticizer and fish oil dispersant. The weight ratio of PVA: DBP: PEG: fish oil is 1: 1: 1: 1 with

FIGURE 3.1: Detailed fabrication process of sintered half-cell from porous NiO-BCZY anode support and spray coated BCZY electrolyte.

1 wt.% to ethanol solvent in total. The solid powder has 5 wt.% to ethanol solvent. The mixture was ball-milled overnight to obtain dispersive and stable suspension. The desirable electrolyte thickness was obtained by repeating the spray coating, with each spray coating cycle applied after the solvent of previously deposited layer was evaporated. After completing the spraying process, the sample was kept in ambient atmosphere for 30 minutes to stabilize the layers before sintering.

The spray coated half cells were first heated from room temperature to 300 °C for 30 minutes with a ramping rate of 2 °C/min, and then heated to 600 °C with the same ramping rate and held there for 1 hour more. Finally the temperature was increased to target temperature with 5 °C/min. For the electrolyte without ZnO,

it was annealed at 1400 °C for 6 hours or 1500 °C for 3 hours, while for that with ZnO sintering aid, it was held at 1400 °C for 4 hours; the sintered half cells are denoted as cell-1400, cell-1500 and cell 1400-ZnO, respectively. After sintering, the half cells were cooled to room temperature inside the furnace.

3.1.3 Fuel cell fabrication

The cathode powder was the mixture of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ (LNCO) and BCZY was prepared by mechanical mixing method. LNCO was prepared by a simple solid-state reaction (SSR) method with $\text{LiOH}\cdot\text{H}_2\text{O}$, $\text{NiCO}_3\cdot 2\text{Ni}(\text{OH})_2\cdot 3.45\text{H}_2\text{O}$, and $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ as the raw materials. The precursors were thoroughly ball milled and annealed at 900 °C for 2 h. LNCO catalyst was used due to its unique triple-conducting (proton, oxygen ion, and electron) property under fuel cell operating condition, which increased the triple phase boundary length for cathode reactions [38, 70, 71]. The LNCO-BCZY mixture was prepared by mechanical mixing of LNCO with BCZY in weight ratio of 3:2. The LNCO-BCZY powder was blended with organic Terpineol based ink vehicle and brush painted on electrolyte surface with an active area of 0.5 cm^2 followed by annealing at 1100 °C for 2 hours.

3.1.4 Material characterizations

The crystallinity of the synthesized BCZY powder were analyzed by X-ray diffraction (XRD, PANalytical Empyrean system) in the range of 20-80° using $\text{CuK}\alpha$ radiation with a step size of 0.01°. The morphologies of the synthesized powder,

the electrolyte surface, the electrolyte/electrode cross-section and interfaces were characterized using a field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7600F). The element distribution of the electrode/electrolyte interface was recorded by an equipped energy-dispersive X-ray spectroscopy (EDX) analyzer in SEM mode.

3.1.5 Characterization of electrochemical performance

The fuel cell was sealed with an alumina on anode side with the ceramic sealant (Aremco 552). Platinum paste annealed at 900 °C with the addition of Pt mesh and Pt wire were used as current collectors. The cathode side was exposed to ambient air. The sample was then kept in a furnace and heated up from room temperature to 650 °C and stabilized for 30 minutes. Pure H₂ was introduced to anode for in-situ reduction for at least 2 hours. The hydrogen flowing rate as 50 ml/min at STP and was moisturized with 3 vol.% of water by passing hydrogen through water tank at room temperature. Fuel cell i-v curves and electrochemical impedance spectroscopy (EIS) characteristics were performed at the temperature range of 650 °C and 550 °C with a decrement of 50 °C on Autolab electrochemical potentiostat (PG30/FRA system, Eco Chimie, Netherlands). The I-V curve was obtained at a scan rate of 0.05 V/Second. And EIS was recorded at the applied frequency range of 100 kHz to 0.1 Hz with ac amplitude of 20 mV. The obtained EIS curves were analyzed on the Zview software (Scribner Associates Inc.) to better understand the detailed electrode reactions and quantitatively determine each contribution to the internal total resistances. The conductivity of spray coated,

anode supported thin film was measured in $\text{H}_2/\text{H}_2\text{O}$ (3 vol.% H_2O) atmosphere with Pt paste as the second electrode. It was extracted from EIS measurement results at the temperature range of 650-450 °C.

3.2 Chemical solution deposition of BZY thin films

3.2.1 Fabrication of BZY thin film by aqueous sol-gel process

An aqueous nitrate sol-gel route combined with a spin coating technique was developed for the deposition of sub-micrometer BZY20 thin films. A systematic study was performed to optimize the process parameters including annealing temperature, sol concentration and heating rate, and investigate their effect on the resulted phase and microstructure of the BZY thin films.

The BZY sol was prepared by an aqueous sol-gel synthesis route. $\text{Ba}(\text{NO}_3)_2$, $\text{ZrO}(\text{NO}_3) \cdot x\text{H}_2\text{O}$, and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were used as starting salts. Citric acid (CA) and ethylenediaminetetraacetic acid (EDTA) were used as chelating agents. Stoichiometric amounts of nitrate precursors were dissolved in deionized water, and CA and EDTA were added at a ratio of 1:0.5:1 to the total metal cations. NH_4OH was added into the solution to adjust the pH value to around 7 and produce a transparent solution. Then the solution was heated at 70 °C under continuous stirring to evaporate the water. By stopping the evaporation at different points, sols

for thin film deposition were obtained with different metal cation concentrations (0.5 M, 0.8 M, and 1.2 M). The remaining solution was stirred until it changed to a viscous gel. The gel was then dried in an oven at 200 °C for 3 hours to obtain the as-dried powders. The as-dried powders were annealed at 800 °C to 1000 °C for 2 hours to investigate the temperature required for the BZY phase formation.

A 500 μm thick Si(100) wafer with 200 nm thick Si_3N_4 coatings on both sides was used as the substrate for the deposition of film. Before deposition, the $\text{Si}_3\text{N}_4/\text{Si}$ wafer was treated under O_2 plasma cleaning for 10 seconds to improve the adherence of the aqueous solution. The sol was dripped on the substrate and spun at a rate of 4000 rpm for 30 seconds using a G3-8 spin coater (SCS Specialty Coating Systems). The as-prepared films were dried in an oven at 150 °C for 20 minutes, and then annealed at 800 °C to 1000 °C in air atmosphere for 2 hours with different heating rates (1 to 5 °C/min) to obtain BZY thin films.

3.2.2 Gas-tight BZY thin film electrolyte on anode substrate

3.2.2.1 Preparation of BZY solution

The chemical solution of BZY film was prepared by dissolving barium acetate (Ba-ac), zirconium acetate (Zr-ac), yttrium nitrate (YNO_3), acetylacetone (A-cac), polyvinylpyrrolidone (PVP, m.wt.: 130,000), and polyethylene glycol (PEG) (Sigma Aldrich, Singapore) in a common solvent of acetic acid. Firstly, Ba-ac was dissolved in acetic acid at 110 °C. After the solution was cooled down to room

temperature, Zr-ac, Acac, YNO_3 , PVP and PEG were added to Ba-ac solution. Ethanol was added to improve the wettability of the solution to the anode substrate; the ratio of ethanol to acetic acid was 3:5 by volume. The solution had the strength of 0.6 M.

To control the shrinkage and prevent crack in BZY film on BZY-NiO anode after sintering, BZY nanoparticles were dispersed into the solution. The BZY powder was obtained via calcining a part of the above solution at 800 °C. The calcined BZY powder was ball milled with 42 wt.% of PVP (m. wt.: 10,000) for 24 hours to minimize the particle size, where PVP plays the role of dispersant for the milled particles. The ground particles, as 10 wt. % of BZY within the solution, were then added to the chemical solution. The particles with the average size range of 0.5 -1.5 μm were further ground to the size below 150 nm using an ultrasonic probe for 30 minutes for better dispersion. The flow chart for the colloid solution preparation is presented in Figure 3.2.

3.2.2.2 Fabrication of BZY Films

The solution with the dispersed BZY nanoparticles was deposited on both Si_3N_4 passivated Si and polished BZY-NiO anode substrates by spin coating at a spinning rate of 4000 rpm for 20 seconds. After coating, the films were baked in oven at 300 °C for 10 minute to remove a part of the organics for the spin coating of the subsequent layers. Repetitions of spin coating and oven baking were performed for 4 cycles to obtain a film of around 500 nm thickness after sintering. The baked

FIGURE 3.2: Flow chart of colloid solution preparation.

films were then sintered at several different temperatures from 600 to 1000 °C for 2 hours for densification and further characterizations.

3.2.2.3 Electrochemical Study

A button cell was fabricated by spin coating BZY nanoparticle-dispersed solution onto a sintered BZY-NiO anode substrate, followed by sintering of the electrolyte film at 1000 °C. The cathode was printed by brush painting of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) on BZY electrolyte and sintered at 800 °C. The thickness of the LSCF cathode was about 20 μm . The OCV of the button cell was recorded at 450 °C using an electrochemical potentiostat (Autolab PGSTAT302)

with pure hydrogen and air supplied as fuel and oxidant, respectively. In-situ reduction of the anode was carried out overnight at 400 °C in pure hydrogen before OCV was recorded.

3.2.3 Rapid thermal processing of chemical-solution-deposited

BZY thin film

3.2.3.1 Preparation of BZY solution

Barium acetate, zirconate acetate in dilute acetic acid, and yttrium nitrate were used as precursors. N,N-dimethylformamide (DMF), water and ethanol were used as solvents. Acetylacetone was added as complexing agent. After mixing the precursors and solvents, a few drops of ammonium hydroxide were added to obtain transparent solution; pH of the solution was adjusted to 4. The volume ratio of DMF:Etanol:H₂O:Acac is 12:4:1:3. The cation concentration of the solution was 0.625 M. The flow chart for the solution preparation is illustrated in Figure 3.3.

3.2.3.2 Fabrication of BZY thin film

Single crystal sapphire ((0001) orientation) wafers were used as substrates for BZY thin film deposition. The substrates were spin coated with chemical solution at the speed of 3000 rpm for 60 s. After that, the coated substrates were dried on a hot plate at 300 °C for 10 minutes to allow pyrolysis. Subsequently, the samples were rapidly sintered in a pre-heated tube furnace. Processing time and temperature

FIGURE 3.3: Flow chart of solution preparation.

were varied for parameter optimization. For comparison, conventional sintering with ramping rate of 10 °C/min was also carried out.

3.2.4 Characterizations of solution and films

The stability of the solution was characterized by Fourier transformed infrared (FTIR) spectroscopy in transmittance mode in the range of 4000 to 500 cm^{-1} at room temperature. The weight loss characteristic of the solution was determined by thermogravimetric and differential thermal analysis (TG/DTA, TA Instruments Q500 Thermogravimetric Analyzer) from room temperature to 750 °C with a heating rate of 10 °C/min in an air atmosphere. The crystallinity and

structural phase of the deposited films were analyzed by grazing incidence X-ray diffraction (GIXRD, PANalytical Empyrean system). The XRD patterns were measured in the range of 2θ of $0.21.0^\circ$ with a constant glancing incident angle at 1° . The thin film densities were determined by X-ray reflectivity (XRR) using the same equipment. Samples were scanned in the 2θ angle of $0.21.0^\circ$. The XRR results were analyzed by X'Pert Reflectivity software. The surface and cross-section morphologies of the films were observed by FE-SEM. The compositions of the films were examined using X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra) with monochromatic Al $K\alpha$ (1486.71 eV) X-ray radiation (15 kV/10 mA).

Chapter 4

Spray Coating of Dense

Proton-conducting

$\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_3$ Electrolyte for

LT-SOFCs

As stated in Chapter 2, fabrication challenges originating from the refractory nature of most proton-conducting electrolytes have hindered their development [11]. Alternative, economic electrolyte membrane fabrication techniques are urgently needed for proton-conducting SOFCs. Spray coating can serve as an option for large size cell preparation and has potential for high quality and high performance. However, there is no demonstration on using the simply direct spray coating method to fabricate a dense proton-conducting membrane on a porous anode substrate. The optimizations of the sintering process as well as the electrochemical

properties have not been characterized yet. Although one can raise the sintering temperature high enough to ensure the densification of electrolyte membrane, the barium evaporation, the coagulation of porous anode microstructures [72], as well as the unwanted chemical reactions between cell components [73] make it desirable to stay at lower sintering temperatures.

In this chapter, the fabrication of a dense proton-conducting electrolyte membrane by a simple direct spray coating is presented with reduced sintering temperature. $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_3$ (BCZY), a proton-conducting ceramic with sufficient conductivity and reasonable chemical stability toward acid gas erosion, was chosen as electrolyte material in this study. The effects of sintering temperature on the electrolyte membrane and anode microstructure, proton conductivity of the resulted thin films, and their fuel cell performances in H_2/air were investigated. Dense BCZY membranes with improved anode microstructure and good proton conductivity have been successfully obtained at reduced temperature using ZnO sintering aid. SOFCs using spray-coated electrolyte thin films gave a stable OCV value of 1.03 V and a maximum power density of 362 mW/cm^2 at 650°C when operated using hydrogen as fuel.

4.1 Crystal structure and morphology of BZCY powder

High annealing temperature is required for forming the desirable phase because of the high decomposition temperature of BaCO_3 (950°C) [73], which was yielded

during co-precipitation process with $(\text{NH}_4)_2\text{CO}_3$ as precipitant. The XRD pattern of BCZY sample heat-treated at 1100 °C for 3 h is shown in Figure 4.1. All the crystal phase peaks can be indexed to BaCeO_3 phase according to the PDF card number 75-0437, but with the peaks slightly shifted due to the different ionic radiuses between Ce (III/IV) and Y (III)/Zr (IV). The calculated crystalline size is around 18 nm by Debye-Scherrer method, while the SEM image (inset picture) shows a typical agglomeration of BZCY powders with an average grain size of 100 nm.

FIGURE 4.1: (a) XRD pattern and (b) SEM image of BCZY powder prepared by $(\text{NH}_4)_2\text{CO}_3$ co-precipitation method. The average particle size is 100 nm.

4.2 Half-cell microstructure

4.2.1 Electrolyte surface

The electrolyte surface microstructures of various cell sintered at different condition are shown in Figure 4.2. It can be seen from Figure 4.2a that though the particles are packed well with each other and presented a smooth surface, some pinholes still exist after annealing at 1400 °C without ZnO sintering aid. Intentionally increased the dwelling time did not change the microstructure too much. The cells sintered at higher temperature (1500 °C for 3 hours) showed the clear gas impermeable surface (Figure 4.2b). However, a close look of the electrolyte surface (Figure 4.2c) showed that partial rough grain surfaces are presence after sintering. This should be caused by the Barium evaporation at the elevated temperature leading to the ceria enriched phase. Therefore, the sintering temperature should not be surpassed 1500 °C in case of the Ba evaporation problem.

An attempt to reduce the sintering but get enough densification was performed by adding ZnO sintering aid into the electrolyte powder. The sintering electrolyte surface microstructure is presented in Figure 4.2d. Distinctively, the samples with sintering aid present a perfect microstructure: smooth surface and well-packed grains after sintered at 1400 °C for 4 hours, which means well-preserved crystal phase and composition. Especially, the average grain size was grown to about 5 μm , much bigger than that of ZnO free samples ($<3 \mu\text{m}$) even at higher sintering temperature (1500 °C). The larger grain size additionally benefits the BCZY

FIGURE 4.2: SEM images of spray coated BCZY electrolytes after being annealed at different temperatures with or without 1 wt.% ZnO sintering aid: (a) cell-1400, (b) cell-1500 and (c) the enlarged cell-1500, and (d) cell 1400-ZnO.

membrane: enhanced ionic conductivity by decreasing the grain boundary contribution from the total resistance [74]. The results clearly show the feasibility of densification of spray coated BCZY electrolyte at lowering temperature with the assistance of sintering aid, ZnO, by simple spray coating method. An attempt to further reduce the sintering temperature down to 1300 °C was failed, which led to apparently porous electrolyte surface.

In open literature, the application of sintering aids, such as Li_2O , LiF , Al_2O_3 , and transition metal oxides, like NiO , CuO , and ZnO [29, 75], have been successfully demonstrated as an effective approach to reduce the sintering temperature of ceramic materials, including the electrolyte materials for SOFC [11, 25], but without

significantly change the their electrical properties. This work again demonstrated the effectiveness of the sintering aid functionality.

4.2.2 Anode/electrolyte interface

SEM images of the microstructure of anode and anode/electrolyte interface microstructure after more than 2 hours in-situ reduction are presented in Figure 4.3. In both cases, the electrolyte layers are bonded well to the anode substrate (Figure 4.3a and b). However, clearly different microstructures have been observed: flat anode internal surface, lower porosity and larger cermet particle size for 1500 °C sintered samples, while higher porosity with well-preserved macropores resulted from pore formers, smaller cermet particle size, and rough reduced Ni surface in the 1400 °C sintered sample with ZnO sintering aid, as shown in Figure 4.3c and d. The higher temperature treatment has induced the structure subsidence even with the active carbon porous former. Insufficient porosity also resulted in low reduction rate due to the difficulty of H₂ diffusion through the anode. For the cell sintered at 1400 °C with ZnO sintering aid, both the macro-pores and the micro-pores were presence; this will ensure the quick gas diffusion and good electrode reaction rate as well as electronic conduction, and consequently higher electrode activity and smaller electrode ohmic resistance.

An energy-dispersive X-ray spectroscopy map scanning analysis (see Figure 4.4) was performed across the anode/electrolyte of the half-cell before anode reduction to examine the elemental diffusion issue between the electrolyte and NiO-based cermet anode after sintered at 1400 °C for 4 hours. No Ni element diffusion into the

FIGURE 4.3: Comparison of the anode/electrolyte interfaces (a, b), and anode microstructure (c, d) sintered at different temperatures: (a, c) cell-1500 and (b, d) cell-1400-ZnO, respectively.

electrolyte was observed. Ba and Ce showed similar trend of content in electrolyte and anode, but showed higher content (brighter) in the electrolyte compared to that in the anode due to composting of BZCY with NiO in anode.

4.2.3 Electrolyte conductivity

The electrical conductivity of spray-coated BCZY electrolyte sintered at 1400 °C with ZnO sintering aid using Pt cathode was tested in humidified H₂ atmosphere. The Arrhenius curve of the electrolyte conductivity is presented in Figure 4.5. The conductivity of BCZY was 0.0102 Scm⁻¹ at 650 °C and 0.0046 Scm⁻¹ at 450 °C,

FIGURE 4.4: EDS map scanning analysis of elemental depth distribution for Ba, Ce, O, Y and Ni on the half-cell before reduction of cell-1400-ZnO.

which are comparable with literature values [25, 76, 77]. The activation energy was 0.31 eV, which is close to the 0.36 eV in a humidified 4% H_2/Ar of Zuo's work [25] and 0.306 eV in fuel cell atmosphere of Peng's study [78] with the same material composition. Such a low activation energy also suggests the proton conducting nature of the spray coating prepared BCZY thin film in H_2/H_2O atmosphere.

4.3 Fuel cell performances and EIS characteristics

The voltage and power density versus current density characteristics of single cells with LNCO-BCZY cathode under different temperature are shown in Figure 4.6. All cells showed open circuit voltages (OCVs) higher than 1.0 V at tested temperatures regardless of the half cell sintering temperature, suggesting the

FIGURE 4.5: Arrhenius curve of porous anode supported BCZY thin electrolyte (cell-1400-ZnO) with Pt cathode.

densification of electrolyte layer and pure ionic conducting nature of BCZY electrolyte. For the cells with the anode/electrolyte sintered at 1500°C , the current density and peak power density were enhanced with the increase of temperature, from 0.7 A/cm^2 , 185 mW/cm^2 at 550°C to 1.1 A/cm^2 , 268 mW/cm^2 to 650°C , respectively. When the cell was sintered at a lower temperature of 1400 with the assistance of $1 \text{ wt.}\%$ ZnO sintering aid, the short current density and maximum power output increased to 1.4 A/cm^2 and 362 mW/cm^2 at 650°C . The higher electrochemical performances at the reduced sintering temperature probably justified that the improved anode microstructure lead to the increased power density.

Figure 4.7 shows the Nyquist plot of EIS results of fuel cells using electrolytes with

FIGURE 4.6: I-V and I-P characteristics of single cell Ni-BCZY/BCZY/BCZY-LNCO in hydrogen/air condition at different temperatures. The cells were sintered at 1500 °C for 3 hours. The optimal cell with 1wt% of ZnO was sintered at 1400 °C for 4 hours.

or without ZnO sintering aid under OCV condition. The fuel cells using BCZY electrolyte without ZnO sintering aid gave electrode polarization resistances of 0.36 and 0.62 $\Omega\cdot\text{cm}^2$ at 650 and 550 °C, respectively. The electrode polarization resistance was mainly from cathode due to the much more sluggish cathodic ORR kinetics than anodic reactions at such low temperatures [79].

However, among the total polarization resistance, a significant portion was attributed to the ohmic resistance at those temperatures, 0.62 and 0.86 $\Omega\cdot\text{cm}^2$ at 650 and 550 °C, respectively. Theoretically, the ohmic resistance for 20 μm electrolyte should be only about 0.21 Ω based on the ionic conductivity of the prepared thin film. In other word, the high ohmic resistance observed here in the EIS results

FIGURE 4.7: Complex electrochemical impedance spectra of different SOFCs under hydrogen/air atmosphere and OCV condition. The cathode is BCZY-LNCO. The last numbers of legends are the fuel cell running temperature, unit $^{\circ}\text{C}$.

means the anode has contributed significantly to the overall ohmic resistance. The insufficient porosity, sintering and low reduction content of NiO in the anode and Barium evaporation issue of the electrolyte as demonstrated in Figure 4.2b and c rendered such an unexpected consequence. With a slight reduction of the sintering temperature by application of ZnO sintering aid, both the series resistance and electrode polarization resistance were reduced to $0.33 \Omega \cdot \text{cm}^2$ and $0.28 \Omega \cdot \text{cm}^2$, respectively (Figure 4.7). The reduction of ohmic resistance, which is almost half of the high temperature sintered cells, is more significant compared with the decrease of electrode polarization resistance. Both optimal values contribute to the excellent fuel cell performance in H_2/air condition, i.e. $362 \text{ mW}/\text{cm}^2$ at 650°C , which is comparable or higher than current most studied oxide cathode materials with the similar fuel cell configuration [80–83].

The cross-section microstructure SEM images of whole cell and cathode after fuel cell performance characterization are shown in Figure 4.8. The electrolyte remained dense with scarce closed pores. The underneath cathode, about $30 \mu\text{m}$

in thickness, and above anode layer are adhered tightly to the electrolyte layer with sufficient porosity (right image), which are highly desirable for the reactant/product gas quick diffusion, surface exchange and provide enlarged triple phase boundaries for electrochemical reactions and quick charge transfer between electrode and electrolyte.

FIGURE 4.8: SEM images of cross-section of cell-1400-ZnO with BCZY-LNCO cathode after fuel cell performance testing, (left) whole cell and (right) cathode.

4.4 Chapter Summary

Dense proton-conducting BCZY electrolyte was successfully fabricated on the porous anode substrate by a single-step spray coating technique at a reduced temperature of 1400 °C with the aid of ZnO. Higher sintering temperature, 1500 °C for 3 h, caused the anode sintering and electrolyte phase separation/Barium evaporation issues, which lead to unexpected large ohmic and anode polarization resistance. Half cells sintered 1400 °C with ZnO showed well-preserved macropores and easily reduced anode microstructure as well as smooth electrolyte surface;

those are highly important for achieving excellent fuel cell electrochemical performance. Fuel cells with brush painted $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ -BCZY composite cathode presented an OCV, peak power density and total electrode polarization resistance of 1.03 V, 362 mW/cm² and 0.28 $\Omega\cdot\text{cm}^2$ at 650 °C, respectively, with hydrogen as fuel. The good fuel cell performances are ascribed to dense and highly ionic conductive electrolyte, the optimized anode microstructure and active cathode catalyst. The results demonstrated that, combining of sintering aid approach, the spray coating method could be a simple and effective approach to fabricate dense proton conducting membrane for solid oxide fuel cell efficient energy conversion at the reduced temperature range.

Chapter 5

Fabrication of Y-BaZrO₃ Thin

Films with Sub-micrometer

Thickness by Chemical Solution

Deposition

The previous chapter demonstrates the development of micrometer scale electrolyte membrane fabrication process based on powder sintering, which is applicable for anode-supported SOFCs. The powder-based techniques still require high sintering temperatures up to 1400 °C even using sintering aids, and the resulted films are generally thicker than 10 μm to obtain pinhole-free and gas-tight electrolyte. In other aspect, vacuum deposition techniques, such as atomic layer deposition [35, 46], pulsed laser deposition [45, 47], and co-sputtering [84] have been demonstrated to produce dense and high quality films in sub-micrometer to tens

of nanometer scales. However, these techniques are costly and require sophisticated equipment set up, and the process is time consuming. In contrast, chemical solution deposition (CSD) is a non-vacuum method to fabricate thin films at low processing temperature with a good control of composition and structure [66]. Due to the cost-effectiveness and scalability, it is a promising way for mass production of electrolyte thin films. In this chapter, CSD technique was developed for the fabrication of yttrium-doped barium zirconate (BZY) thin films.

Firstly, a sol-gel process was developed for the fabrication of sub-micrometer scale BZY thin film at much lower processing temperatures than conventional solid-state sintering. A systematic study was performed to investigate the process parameters including annealing temperature, sol concentration and heating rate, and the resulted phase and microstructure of the BZY thin films was characterized.

Subsequently, an acetate based chemical solution was developed to fabricate gas-tight BZY electrolyte thin film on BZY-NiO anode substrate. The CSD method modified with the dispersed BZY nanoparticles and with a carefully controlled sintering schedule effectively eliminates the drying and constraint sintering cracks of the thin film. This modified method is capable of producing crack-free, polycrystalline, single phase and stoichiometric BZY thin film at a low temperature of 1000 °C. The gas-tightness of the film was verified through the open circuit voltage (OCV) experiment on a button fuel cell, which is the first successful electrochemical measurement reported for sub-micrometer thin BZY electrolyte fabricated by CSD process.

Thirdly, rapid thermal processing (RTP) was explored as alternative sintering strategy to lower the sintering temperature and suppress barium evaporation and interfacial reaction. The low annealing temperature and shorter processing time allow the incorporation of chemical solution deposited BZY thin films into the practical micro-SOFC application. The combination of CSD method and RTP can be a promising alternative to vacuum-based thin film deposition techniques for the fabrication of nanoscale BZY electrolyte thin film.

5.1 BZY thin film fabricated from aqueous sol-gel route

This section demonstrated the deposition of sub-micrometer $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZY20) thin films by a sol-gel route combined with a spin coating technique. An aqueous nitrate based solution was developed for BZY thin film fabrication. A systematic study was performed to investigate the process parameters including annealing temperature, sol concentration and heating rate, and the resulted phase and microstructure of the BZY thin films was characterized.

5.1.1 BZY phase formation

5.1.1.1 Influence of annealing temperature

The XRD patterns of powders shown in Figure 5.1(a) indicates the desired perovskite phase appeared at a temperature as low as 800 °C, but with small peaks

that shows the existence of barium carbonate residue. After annealing at 1000 °C for 2 hours, all peaks corresponding to barium carbonate phases disappeared and a pure phase of BZY was obtained. The BZY films with a sol concentration of 0.8 M deposited on Si₃N₄/Si substrate (shown in Figure 5.1(b)) exhibited the same trend as the powders. No additional peaks were observed in the XRD result, indicating reaction between BZY film and substrate did not occur in this temperature range.

5.1.1.2 Influence of sol concentration

The effect of sol concentration on BZY phase formation was further studied. Figure 5.2 shows XRD patterns of thin films deposited with sol concentrations of 0.5 M, 0.8 M and 1.2 M, all annealed at 1000 °C for 2 hours. For the film deposited with a sol concentration of 0.5 M, no obvious diffraction peaks were detected. When sol concentration increased to 0.8 M, BZY phase formation was observed and for sol concentration of 1.2 M, the intensity of the diffraction peaks further increased. At a low concentration of 0.5 M, the large distance between the reacting species hindered the formation and growth of the network to form BZY. At a higher concentration up to 0.8 M, cross-linked network was formed and BZY crystalline phase appeared. The increase of the detected peak intensity with 1.2 M concentration can be attributed to the increase of the film thickness due to the higher sol viscosity [85]. Thus, sols with a concentration of 0.8 and 1.2 M were chosen for subsequent microstructure characterization and optimization.

FIGURE 5.1: XRD patterns of (a) powders and (b) thin films deposited with sol concentration of 0.8 M annealed at 800, 900, and 1000 °C.

5.1.2 Thin film microstructure

5.1.2.1 Influence of sol concentration

Highly dense and pinhole-free thin film electrolyte is desirable for high open circuit voltages and stable cell performance during SOFC operation. Figure 5.3 shows the SEM images of the surface and cross-sectional structure of BZY thin films

FIGURE 5.2: XRD patterns of thin films deposited with sol concentrations of 0.5 M, 0.8 M and 1.2 M, annealed at 1000 °C for 2 hours.

deposited on $\text{Si}_3\text{N}_4/\text{Si}$ substrate with sol concentrations of 0.8 M and 1.2 M, and annealed at 1000 °C for 2 hours with a ramping rate of 5 °C/min. The film deposited from 0.8 M sol showed less surface cracks and better adhesion to the substrate. From cross-sectional SEM view, the film was about 200 nm thick, and no obvious through-film cracks or interconnected pores were observed. For the film deposited from 1.2 M sol, the film thickness increased to 400 nm, and through-film cracks were clearly observed. The formation of the cracks can be attributed to the large thermal stress between the BZY film and the $\text{Si}_3\text{N}_4/\text{Si}$ substrate due to the difference in thermal expansion coefficients. Since the thicker films tend to be less tolerant to such a mismatch, 1.2 M film showed more evident cracks. Thus, the sol with a concentration of 0.8 M was selected for further experiments.

FIGURE 5.3: Surface and cross-sectional FE-SEM images of thin films deposited with sol concentration of (a, b) 0.8 M, (c, d) 1.2 M, respectively.

5.1.2.2 Influence of heating rate

During annealing, the heating rate affects the speed of organic decomposition, which can also induce shrinkage and cracks in the microstructure. In order to minimize surface cracking, the heating rate was reduced from 5 °C/min to 1 °C/min during annealing. Figure 5.4 shows surface micrographs of the BZY thin films deposited with 0.8 M sol and annealed at 1000 °C with different heating rates. It can be observed that reducing the heating rate lowered the incidence of cracks and the thin film heated with a ramping rate of 1 °C/min had the fewest cracks and smoothest surface after annealing, since the lower heating rate led to slower organic decomposition and less shrinkage.

FIGURE 5.4: Surface FE-SEM images of BZY thin films annealed with different ramping rate: (a) 5 °C/min, (b) 2 °C/min, (c) 1 °C/min.

5.1.3 Thin film composition

The composition of the BZY thin films fabricated with the optimized parameters (sol concentration of 0.8 M, annealing temperature of 1000 °C, and heating rate of 1 °C/min) was examined by XPS, shown in Figure 5.5. The atomic ratio of Ba, Zr and Y was 1: 0.82: 0.22, close to the nominal ratio of 1: 0.8: 0.2. This means the sol-gel process is capable of maintain the composition of BZY thin film. No obvious Ba evaporation occurred due to the much lower processing temperature of 1000 °C, and therefore a high conductivity for the BZY thin film deposited by the sol-gel spin coating method can be expected.

5.1.4 Summary

Sub-micrometer BZY thin films were fabricated at a low processing temperature with the combination of sol-gel and spin coating method. BZY single phase without barium carbonate residue was obtained with a low annealing temperature of 1000 °C. 200 nm-thick BZY thin film with surface cracks but without obvious through-film cracks was fabricated with the optimized process parameters of the sol concentration of 0.8 M and heating rate of 1 °C/min. No Ba evaporation

FIGURE 5.5: XPS spectra of BZY thin film deposited from 0.8 M sol annealed at 1000 °C with 1 °C/min heating rate. The atomic concentration of each element is shown in the inserted table.

was detected due to the low temperature annealing. Integrating the advantages of easy fabrication and good control of the composition, the sol-gel spin coating process can be a low-cost method without vacuum environment for deposition of sub-micrometer thin film.

5.2 BZY thin films fabricated on anode substrates

In this section, a 500 nm thick BZY electrolyte film was fabricated on the BZY-NiO anode substrate at a remarkably low temperature of 1000 °C by CSD method. In order to eliminate the drying and constraint sintering cracks of the thin film, the chemical solution was modified with the dispersed BZY nanoparticles and the

sintering schedule was carefully controlled. Gas-tightness of the BZY film was confirmed by stable OCV at 1.08 V from a button fuel cell with NiO-BZY anode substrate and LSCF cathode.

5.2.1 Optimization of BZY Solution

One of the challenges to deposit BZY thin film with CSD is the adhesion between the film and the substrate, which depends on the wettability of the solution and substrate. Therefore, in this study, the wettability of the BZY solution was optimized with non-aqueous solvents. The primary solvent of this solution was an acetic acid which has a surface tension of 25.71 mN/m at 30 °C. In the mixed solution, the presence of water was necessary to ensure complete dissolution of Y-nitrate and to facilitate network formation through partial hydrolysis. However, since the surface tension of water is 71.21 mN/m at 30 °C, which is too high to wet the substrate, ethanol with a lower surface tension of 21.41 mN/m at 30 °C was added to the solution. The ratio of water and ethanol was maintained in such a way that the mixture gives the similar value of surface tension with that of acetic acid.

The stability of the solution was confirmed by taking FTIR spectrum for the fresh solution and one month after it was formulated. Figure 5.6 shows the FTIR spectra of both the fresh solution and the solution aged for one month. Two spectra overlap each other. The functional group region shows that both the solutions have same functional group, while the overlapped fingerprint region demonstrates

no distortion in metal-oxygen coordination within one month of time. The result indicates the solution was stable for month.

FIGURE 5.6: FTIR spectra showing the stability of the formulated BZY solution over time.

5.2.2 Phase and Crystallinity of Films

Figure 5.7 shows the XRD patterns for BZY films on anode substrates, sintered at various temperatures between 600 and 1000 °C. For the film sintered at 600 °C, no clear peak was observable. The film sintered at 700 °C showed peaks with the presence of unwanted BaCO_3 phase. At 800 °C distinct peaks appeared without peak splitting, showing the absence of phase separation issue which is common for BZY sintered at 1450 °C and above [29]. In addition, the unwanted BaCO_3 peak is not observed. For the films sintered at higher temperatures, the peak intensity increased, indicating better crystallinity of the film was obtained. In short, the process was successful to produce polycrystalline and single phase BZY

without observable second phase at temperature as low as 800 °C, while solid state processes can produce single phase BZY only at 1100 °C or higher [86].

FIGURE 5.7: Crystallinity development of sintered BZY films with temperature.

5.2.3 Sintering of BZY Film

The films deposited on BZY-NiO anode substrate were sintered at different temperatures of 800, 900 and 1000 °C (Figure 5.8(a-c)). Due to the different thermo-mechanical properties of BZY film and BZY-NiO anode, the sintering of BZY film on BZY-NiO anode requires careful control of sintering schedule and formulation of solution to minimize the constraint sintering effect.

The strategies of sintering schedule include: (1) a slow heating rate of 1 °C/min to eliminate drying crack in the green stage; (2) a faster heating rate of 10 °C/min

to retain OH and OR groups to the temperature higher than the usual temperature for their removal to delay crystallization to facilitate densification before completion of crystallization; (3) a slower cooling rate at high temperature region to relieve the constraint sintering stress [67]. To further confront the constraining effect on the film, BZY nanoparticles were dispersed into the BZY solution to serve as slow sintering inclusion. The dispersed BZY nanoparticles produce a multi-axial stress field within the film during densification. Multi-axial stress fields surrounding the nanoparticles initiates the rearrangement of precursor powder to facilitate even distribution of sintering stress exerted by the substrate and reduce the overall shrinkage rate of the film matrix, alleviating differential shrinkage issue.

The film sintered at 800 °C was extremely porous while porosity reduced at 900 °C (Figure 5.8a, b). The BZY film sintered at 1000 °C (Figure 5.8c) was crack-free and nearly dense with only a very few pores. These few pores are inevitable since the constraint sintering effect of cermet anode substrate cannot be eliminated completely. The heterogeneous microstructure observed on the surface of the BZY film indicates the uneven stoichiometric distribution of elements. EDX spectra were recorded at various spots on the film. Table 5.1 summarizes the compositions at spots 1 and 2 (Figure 5.8c), which shows the consistent stoichiometry. The ratio of elements also confirms the perovskite structure of BZY. The unevenness may be attributed to different nucleation events on the surface of the film and at the interface, and growth kinetics.

FIGURE 5.8: BZY films sintered on anode substrates at (a) 800, (b) 900 and (c) 1000 °C.

TABLE 5.1: Compositional details of BZY surfaces in Figure 5.8c, showing nearly the same compositions of the two spots.

Element	Spot 1	Spot 2
O K	59.22	58.91
Zr L	21.47	20.45
Ba L	19.30	20.64

5.2.4 Verification of Gas-Tightness by OCV

The OCV of the anode-supported button cell was determined to verify the gas-tightness of the sintered BZY film. After overnight reduction of anode in hydrogen gas, a high OCV, close to the theoretical value of 1.15 V, of 1.08 V was obtained. Figure 5.9 shows the OCV of the cell at 450 °C, captured for 2 hours, which proved the gas-tightness of the 500 nm thick BZY film. The OCV was stable for more than 8 hours in the temperature range of 450 to 550 °C. The OCV dropped to 0 V due to delamination of the electrolyte film from anode substrate when the temperature was raised to 600 °C (Figure 5.10(a, b)).

To the best of the author's knowledge, a BZY film with sub-micrometer thickness as fuel cell electrolyte was not yet achieved by a solution-based method. The sub-micrometer thick BZY electrolyte films have only been demonstrated by using vacuum-based methods such as pulsed-laser deposition [47, 49] and atomic layer

FIGURE 5.9: Stable OCV of the BZY fuel cell at 450 °C.

FIGURE 5.10: The cross-sectional view of the layers in the button cell: (a) before OCV test and (b) after test.

deposition [46], which are non-scalable and costly. The solution-based method provides a low-cost and scalable alternative approach to the fabrication of high quality BZY thin film electrolytes with the thickness below micron.

5.2.5 Summary

A gas-tight, sub-micrometer thick BZY electrolyte film, derived via CSD method modified with externally added BZY nanoparticles into the solution, was successfully sintered at a significantly low sintering temperature of 1000 °C. Dense, crack-free, polycrystalline, BaCO₃-free and single phase BZY film was achieved by the simple and low-cost CSD method combined with the carefully planned sintering schedule, which provides the low cost manufacturing process for marketable LT-SOFCs. The stable OCV of 1.08 V for over 2 hours confirmed the gas-tightness of the film.

5.3 BZY thin films sintered by rapid thermal processing

In this section, dense and crack-free BZY thin films were fabricated by CSD with rapid thermal processing (RTP) at low sintering temperature. BZY thin film without BaCO₃ phase was obtainable after annealing at 700 °C for 1 hour, which represents the lowest temperature reported in the literature. X-ray reflectivity study showed that the relative density of resultant BZY thin film was approximately 90%, indicating the effective densification of BZY at low temperature sintering by RTP. Microstructural analysis of BZY thin film showed that the film was dense, smooth and homogenous without cracks or interconnected pores.

5.3.1 Optimization of BZY Solution

By heating with RTP, the film may get disrupted due to the stress generated during solvent evaporation and heat treatment. The film after deposition acts like a viscoelastic solid which entraps solvent in the pores of the network of inorganic cations along with organic moieties. As the solvent evaporates, capillary contraction occurs and generates high capillary pressure, causing differential pressure in the whole network. To reduce the pressure and make it uniform throughout the network, N,N-dimethylformamide (DMF) was used as drying control chemical agent to help in increasing the pore radius within the network of the cations, thereby decreasing the stress [87]. Acetylacetone has been added as a chelating agent to form a good network of cations.

In order to maintain the solution stability over time, the pH value of the solution was adjusted to 4 by adding ammonium hydroxide. Without pH adjustment, the solution cannot be stable for more than 3 to 4 hours. The stability of the solution was confirmed by taking FTIR spectrum for the fresh solution and 2 months after it was formulated. As presented in Figure 5.11, both the functional group region and the finger print region remained unchanged, suggesting the solution remained stable after being formulated for 2 months.

5.3.2 Thermal analysis of BZY solution

Thermal analysis was used to get better understand of the thermal decomposition and the crystallization process with temperature. The TG-DTA curves of the

FIGURE 5.11: FTIR spectra of the fresh solution and 2 months old solution.

BZY solution are shown in Figure 5.12. The curves indicate that major mass loss occurred below 150 °C. The boiling temperatures for the organics in the solution are 78, 153, 118 and 140 °C for ethanol, DMF, acetic acid, and acetylacetone, respectively. Therefore, these substances along with water might have evaporated at this temperature range. The total weight loss up to 150 °C is 68%, which means most of the organics in the solution have been evaporated. Another temperature range where weight loss occurred was 300-360 °C with the amount of weight loss about 6%. This could be attributed to the decomposition of the pyrolysis products and the organic residual. Above 360 °C, no significant weight loss was observed up to 750 °C, which indicates that all the organic species have been removed. The temperature range of 450-700 °C is generally attributed to condensation, structural rearrangement, and crystallization.

FIGURE 5.12: TG/DTA curves of the BZY solution.

5.3.3 Optimization of BZY thin film

The effect of sintering schedule on thin film crystallization was studied by GIXRD. Figure 5.13 presents the XRD patterns of BZY thin films sintered at 600-800 °C for various time periods with RTP. The film sintered at 600 °C only exhibited a broad (110) peak, indicating that an amorphous state was formed. The polycrystalline BZY phase was formed after sintering at 700 °C. The film presented clear perovskite BZY peaks, which agree well with the standard BZY PDF card 96-720-2180. However, an extra peak corresponding to ZrO_2 near BZY (211) peak was observed in the film sintered for 30 minutes due to insufficient reaction time. With longer sintering time of 1 hour, film with pure BZY phase was obtained. Similar phenomenon was observed for the film sintered at 800 °C. Thus, dwelling

time of 1 hour is necessary to obtain pure BZY without secondary phase. It is worth noting that no intermediate BaCO_3 phase was detected for the RTP film. In comparison, as shown in Figure 5.14, the film heated with conventional process had large amounts of intermediate BaCO_3 phase after sintering at 700 °C for 30 minutes. The BaCO_3 phase still cannot be completely decomposed even after sintering for longer time of 1 hour or higher temperature of 800 °C for 30 minutes. Pure BZY phase was formed after sintering at 800 °C for 1 hour by conventional heating process. A possible explanation is provided as follows. In conventional heating process, it is easy for BaCO_3 formation at the temperature range from 600 to 700 °C, which can be observed from the XRD patterns in Figure 5.14. In contrast, when the film was sintered with RTP, the sintering temperature directly reaches 700 °C where BZY crystallization dominates. Therefore, BaCO_3 could be effectively avoided due to a much shorter time in the temperature range favoring BaCO_3 formation (600-700 °C). Moreover, the formed BaCO_3 may quickly react and convert to perovskite BZY phase [88]. In this way, sintering with RTP can yield pure perovskite BZY phase at low temperature of 700 °C.

In order to analyze the densification behavior of the BZY thin films sintered with RTP, XRR method was employed. Figure 5.15 shows typical experimental XRR curves for the BZY thin films after one-layer spin coating and subsequent sintering at 700 and 800 °C for 1 hour with RTP. The XRR results showed that the BZY films had a thickness around 40 nm and a surface roughness about 1-2 nm after one-layer deposition. The relative densities were 90% and 93% for thin films sintered at 700 and 800 °C, respectively. The results indicated that RTP could

FIGURE 5.13: XRD patterns of BZY thin films sintered at 600-800 °C for various time with RTP.

FIGURE 5.14: XRD patterns of BZY thin films sintered at 600-800 °C for various time by conventional heating process.

be an effective way to densify BZY thin film in a short time. The rapid removal of solvent and retardation of crystallization to high temperature can facilitate the densification process at lower temperature, compared to other heating methods [89].

FIGURE 5.15: Typical XRR curves of thin films sintered at 700 °C and 800 °C for 1 hour with RTP.

To study the relationship between microstructure and sintering temperature, the morphologies of BZY films sintered at different temperatures were observed. The studied films had a thickness around 160 nm with four-layer coating. Figure 5.16a and d show SEM surface micrographs of films sintered at 700 and 800 °C at low magnification. Both films exhibited smooth surface morphologies without severe surface cracks, but the film sintered at 800 °C showed relatively inhomogeneous structure compared to the film sintered at 700 °C. Figure 5.16b and e present high magnification SEM surface images of the sintered films. The film sintered at

700 °C had smooth microstructure and uniform grain distribution with the grain size around 20 nm. In contrast, the film sintered at a higher temperature of 800 °C was observed to have grain agglomeration and small size crack defects due to the larger thermal stress. The cross-sectional SEM images (Figure 5.16c and f) indicate that both films sintered at 700 and 800 °C were dense without through-film cracks or interconnected pores. However, the non-uniform surface and crack defects of the film sintered at 800 °C may lead to gas leakage for the nanoscale electrolyte thin film. The film sintered at 700 °C with RTP is more desirable for electrolyte film application. Even though the one-layer coating film has a relative density of 90% determined by XRR, the thicker film after four-layer coating shows dense structure without interconnected pores, as a consequence, it may exhibit more chance to guarantee good gas tightness as electrolyte film [43, 60].

FIGURE 5.16: Surface and cross-sectional FE-SEM images of BZY film sintered with RTP for 1 hour at different temperatures of (a, b, c) 700 °C and (d, e, f) 800 °C.

Subsequently, the composition of BZY film sintered with RTP at 700 °C for 1 hour was analyzed by XPS. From the XPS survey spectra (Figure 5.17a), it was

determined that the atomic composition of BZY film was Ba 19.01%, Zr 14.28%, Y 4.03%, O 62.68%, which is close to the nominal value. Besides, there was no impure element detected in the film. The results showed that the low processing temperature and short heating time can maintain the composition and suppress Ba evaporation. Furthermore, the absence of BaCO_3 phase was confirmed by the narrow scan of Ba3d presented in Figure 5.17b. The Ba3d peaks showed a symmetrical nature and only one group of peaks was detected. The peak at 777.9 eV was identified as signals from Ba-O bonds [90], which is associated with perovskite BaZrO_3 . No signal corresponding to BaCO_3 at higher binding energy of 779.4 eV was found, indicating the absence of BaCO_3 in the film.

5.3.4 Summary

Dense, homogenous and crack-free BZY thin films have been successfully fabricated by CSD method combined with RTP as sintering schedule. Crystallized BZY film without BaCO_3 impurity was obtained at the low processing temperature of 700 °C for 1 hour with well-controlled composition. To the best of the author's knowledge, 700 °C is lower than the reported temperatures for BZY thin film fabricated by CSD. The combination of CSD method and RTP can be a promising alternative to vacuum-based thin film deposition techniques for the fabrication of nanoscale BZY thin film for micro-SOFC application.

FIGURE 5.17: XPS spectra of BZY thin film (a) survey spectra and (b) narrow-scan of Ba3d.

Chapter 6

Conclusions and future work

6.1 Conclusions

In this project, several approaches were developed to address the fabrication problems of BaZrO_3 - BaCeO_3 proton conducting materials and synthesize the electrolyte films with scalable and cost-effective routes. Conclusions are drawn as follows.

1. Dense proton conducting BCZY electrolyte membranes have been successfully fabricated on the porous anode substrates by a single-step spray coating technique at a reduced temperature of 1400 °C with the aid of ZnO. Half cells sintered at 1400 °C with ZnO showed well-preserved macropores and easily reduced anode microstructure as well as smooth electrolyte surface which are highly important for achieving excellent fuel cell electrochemical performance. Fuel cells with LNO-BCZY composite cathode presented an OCV, peak power density and total

electrode polarization resistance of 1.03 V, 362 mW/cm² and 0.28 Ω·cm² at 650 °C, respectively. The good fuel cell performances are ascribed to dense and highly ionic conductive electrolyte, the optimized anode microstructure and active cathode catalyst. The results demonstrated that, combining of sintering aid approach, the spray coating method could be a simple and effective approach to fabricate dense proton conducting membranes for SOFCs at the reduced temperature range.

2. To avert the sintering problem of BZY electrolyte and reduce the film thickness, chemical solution deposition method has been successfully developed for the fabrication of sub-micrometer BZY thin films. CSD method can be a promising alternative to vacuum-based thin film deposition techniques for the fabrication of sub-micrometer thin BZY film electrolytes due to its simplicity, scalability and cost effectiveness. Moreover, CSD is capable of sintering ceramic materials at low temperature, which can effectively suppress Ba evaporation. The specific contributions are concluded as follows.

Firstly, an aqueous sol-gel route has been developed for the fabrication of sub-micrometer BZY thin film at low processing temperature of 1000 °C. 200 nm-thick thin film without obvious through-film cracks was fabricated with optimized process parameters of sol concentration and heating rate. The stoichiometry of the BZY thin film was well-controlled and no Ba evaporation was observed due to the low processing temperature. However, small surface cracks still existed even after parameter optimization. This is due to the large thermal stress during drying and sintering, which can be reduced by further optimization of chemical solution system.

Secondly, a modified chemical solution deposition route has been employed to fabricate dense and crack-free BZY electrolyte thin films. Stable organic chemical solution with the addition of BZY nanoparticles was developed and the sintering schedule was carefully planned to eliminate the drying and constraint sintering cracks of the thin film. BZY thin film electrolyte with a thickness of 500 nm was successfully deposited from colloid solution on anode substrate at a low sintering temperature of 1000 °C. A stable OCV of 1.08 V for the anode-supported fuel cell indicated good gas tightness of the BZY electrolyte thin film.

Thirdly, rapid thermal processing has been proposed as an effective sintering schedule to fabricate dense BZY thin film at low processing temperature. With fast heating rate, nucleation and crystallization processes are delayed to a higher temperature, and densification processes are facilitated prior to the onset of crystallization. Dense, crack-free, and polycrystalline BZY film without BaCO₃ impurity was obtained at low temperature of 700 °C for 1 hour with well-controlled composition. The relative density can reach to 90% as measured by X-ray reflectivity. The low processing temperature and shorter annealing times allow the incorporation of chemical solution deposited BZY thin films into micro-SOFC devices.

6.2 Future work

Several scalable and cost-effective approaches for the fabrication of proton-conducting electrolyte films have been demonstrated in this thesis. In particular, the BZY thin films fabricated by chemical solution deposition is potentially applicable in

the fabrication of thin film SOFCs. To realize the incorporation of chemical solution deposited thin film into SOFCs and improve the fuel cell performance, the following future works are proposed.

- Conductivity study of BZY thin films

In order to obtain accurate conductivity value, BZY thin film with larger thickness and/or interdigitated electrode array will be used for the in-plane conductivity measurement. The BZY thin films grown by CSD can be also used to study the effect of crystallinity and microstructure on proton conductivity. The crystallinity and grain size can be well-controlled by the CSD routes.

- Optimization of anode-supported SOFCs

The anode-supported SOFC based on chemical-solution-deposited BZY electrolyte has demonstrated encouraging OCV value, but the fuel cell performance is poor. The microstructure of the cell showed delamination of electrolyte film from anode and cathode due to the differential shrinkages among the cell components. Thus, constant efforts to optimize the shrinkage and other processing parameters need to be made. The cathode film could be deposited by CSD method to solve the adhesion problem and improve the performance.

- Fabrication of micro-SOFCs

Silicon-based micro-SOFCs can be fabricated by micro-machining techniques such as lithography and etching processes. After deposition of electrolyte membrane,

the silicon-based substrate is etched and obtain a free-standing electrolyte. It is essential to control the stress level of the electrolyte film to ensure the survival of the membrane after etching and maintain good thermomechanical stability. To incorporate the BZY thin film deposited by CSD into silicon-based micro-SOFCs, the stress of electrolyte thin film could be further reduced by the substrate selection.

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Publication List

Journal Papers

1. **Hanlin Xie**, Pei-Chen Su. Fabrication of yttrium-doped barium zirconate thin films with sub-micrometer thickness by a sol-gel spin coating method. *Thin Solid Films*. 2015;584:116-119.
2. **Hanlin Xie**, Mridula Biswas, Liangdong Fan, Yong Li, Pei-Chen Su. Rapid thermal processing of chemical-solution-deposited yttrium doped barium zirconate thin films. *Surface and Coatings Technology*. In Press.
3. Liangdong Fan, **Hanlin Xie**, Pei-Chen Su. Spray coating of dense proton-conducting $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_3$ electrolyte for low temperature solid oxide fuel cells. *International Journal of Hydrogen Energy*. 2016; 41:6516-6525.
4. Mridula Biswas, **Hanlin Xie**, Pei-Chen Su. Low Temperature Synthesis of Sub-micrometer Yttria-doped Barium Zirconate Thin Films by Modified Chemical Solution Deposition Technique. *ECS Transactions*. 2015;68:481-488.
5. Mridula Biswas, **Hanlin Xie**, Jong Dae Baek, Pei-Chen Su. Fabrication of yttria-doped barium zirconate electrolyte with sub-micrometer thickness via low temperature viscous flow sintering. *Surface and Coatings Technology*. In Press.

Conference Presentations

1. **Hanlin Xie**, Mridula Biswas, Yong Li, Pei-Chen Su. Rapid Thermal Annealing of Chemical-Solution-Deposited Yttrium-doped Barium Zirconate Thin Films. *The 8th International Conference On Technological Advances of Thin Films and Surface Coatings*, July 12-15, 2016, Singapore.
2. Mridula Biswas, **Hanlin Xie** and Pei-Chen Su. Low Temperature Synthesis of Sub-micrometer Yttria-doped Barium Zirconate Thin Films by Modified Chemical Solution Deposition Technique. *ECS Conference on Electrochemical Energy Conversion & Storage with SOFC-XIV*, July 26-31, 2015, Glasgow, Scotland.
3. **Hanlin Xie**, Pei-Chen Su. Fabrication of Yttrium-doped Barium Zirconate electrolyte thin films by sol-gel spin coating method, *The 7th International Conference on Technological Advances of Thin Films and Surface Coatings*, July 15-18, 2014, Chongqing, China.